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The "Splash Negative Figure" and the Side-Branches of the Positive Figure impressed on Photographic Plates

By

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Abstract

(1) Discharge-figures were taken on photographic plates, on which a gas-blast was thrown. The blast shows a remarkable effect on the negative figure, while it produces hardly any appreciable change in the form of the positive figure. The "splash negative figure" obtained with the blast is probably mainly due to an irregular distribution of gas-pressure produced by the blast.

(2) Some experiments as to the formation of the side-branches of the positive-figures have been carried out. The results show that the "thorns" produced at the successive new electrodes on the stems have a close relation to the formation of the side-branches, and they are explained by Yoshida's theory.

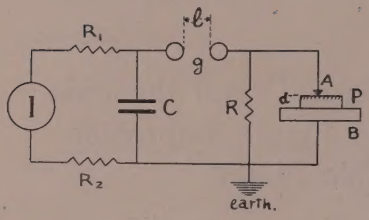
(3) The fact that the spreading-out of the positive figure is greater than that of the negative is experimentally proved to be due to the difference in horizontal intensity of the field at the edges of the positive and negative stems.

CHAPTER I

Introduction

Fig. 1 shows an electrical connection which is used for most of the experiments described below. An electrode A is placed on the sensitive film of a photographic plate P resting on an earthed metal plate B. I is an influence machine or an induction coil whose two terminals are connected with the great resistances R_1 and R_2 respectively. R is another great resistance, C a condenser and g a spark gap whose length is l.

Fig. 1



If an electric impulse resulting from a spark at g reaches the electrode A and its amplitude is sufficient, a discharge-figure is impressed on the plate P. The figures thus obtained depend on the sign of the impulse. The stems of the positive figure have many side-branches, but the negative figure generally has none.

The writer has investigated the character of the side-branches of the positive figure, and reached the conclusion that the appearance of the side-branches is due both to the irregular edges of the stems and the horizontal intensity of the electric field.

CHAPTER II

Influence of Gas-Blast on the Discharge-Figure

J. A. Fleming and H. W. Richardson[1] found that if an air-blast was thrown on the gap, the images of the spark were seen to have a ragged tail or aureole which was blown away from the spark and that the tail was the image of the arc-discharge superimposed on the oscillatory spark. Torahiko Terada and U. Nakaya[2] have investigated the same subject for the "three-part spark" and found that the positive part was easily drifted away, while the middle part (as well as the spark of the zigzag type) was quite insensible to the air-blast, and that the blast upon the negative electrode transformed the spark into brushes. From these experiments, they argued that the "three-part spark" needed a slow preparatory process.

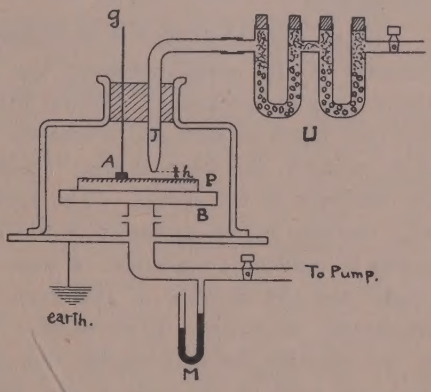
The writer has made some experiments on the effects of a gas-blast on the discharge-figure and found that the negative figures gave remarkable results. The discharge-figures were taken, while a jet of air supplied from an air tank at about 3 atmospheres was thrown by means of a glass jet tube on the portion to be covered by the discharge-figure. Fig. 5 in Plate I is the negative figure affected by the air-blast and we can easily see some distinct thread-like branches in the neighbourhood of the nozzle. However, the positive figure was

1. J. A. Fleming and H. W. Richardson; Phil. Mag. **17**, 677, (1909).
2. T. Terada and U. Nakaya; Sci. Pap. Inst. Phys. Chem. Res., **8**, 103, (1928).

quite insensible to the blast. In order to make the features clearer, the discharge-figures were next taken under low air-pressures, for the lower the pressure of the gas, the broader the stems and the larger the figure itself.

In Fig. 2, the electrode A, the photographic plate P and the earthed metal plate B are enclosed in a sealed bell jar provided with an exhaust arrangement, and both the glass gas-jet tube J of about 4 mm. in diameter and the lead wire g A pass through the rubber stopper. To get rid of dust particles and water vapour, U-tube filters containing $CaCl_2$, each of which is covered with cotton or glass-wool, are connected to the jet-tube. M is a mercury manometer and h shows the distance between the sensitive film of the photographic plate and the nozzle of the jet-tube. Some discharge-figures were taken with various diameters at the nozzle and various values of h, with different pressures of gas in the jar.

Fig. 2



(1) Effect of an air-blast on the positive discharge-figures

The air was removed from the bell jar by an air pump until the pressure was reduced to about 20 mm. Hg. and then the air-blast caused by the difference in pressure between the inside and the outside of the jar was thrown on the photographic plate. The discharge-figures were taken at a moment when the reading of the manometer was about 50 to 70 mm. Hg. With dry and dust-free air, it was found that the form and the structure of the positive figures were almost unchanged, except that there was a somewhat greater number of side-branches, as is shown in Fig. 1, Plate I. However, it was found that, if an air-blast saturated with water vapour was used, remarkable stelliform branches radiated outside from the position under the nozzle as shown by Fig. 2 in the same plate. These stelliform branches were, perhaps, due to the fact that drops of water condensed on the film acted as new positive electrodes.

(2) Effect of the air-blast on the negative discharge-figures

The effect in this case was much more marked. Fig. 6 in Plate I is a negative figure obtained under the following experimental conditions: $l=1.3$ mm., $h=2$ mm., diameter of the nozzle $=1.3$ mm., and the reading of the manometer, at the moment of the impression of the discharge-figure, was about 50 mm. Hg. In this figure, new brushes consisting of a great number of rays with some side-branches appear round the nozzle, but not emanating from the electrode A. We will hereafter call this figure the "splash negative figure" for convenience.

When the value of h is increased, say to 5 cms., by keeping the diameter of the nozzle constant, say 1.3 mm., these rays mentioned above broaden gradually. When further increases are made in h, they get much broader and ultimately disappear. If the value of h is kept constant, the form of the "splash negative figure" depends on the diameter of the nozzle. The rays of the figure broaden a little with increase in the diameter of the nozzle. If the diameter of the nozzle is reduced to 0.2 mm. or less, fine rays appear very near the nozzle, and the number of the rays as well as the range of their appearance decreases. Even when a wet air-blast was used, the form of the negative discharge-figure was generally the same, but stelliform branches, such as are seen in the positive figure, appeared, though they were comparatively weak.

(3) The "splash negative figures" obtained with various gases

Similar experiments were carried out with hydrogen, oxygen, nitrogen and carbon-dioxide, which contained some impurities. After the glass jet-tube had been connected to a gas tank, the discharge-vessel containing the photographic plate, as shown in Fig. 2, was cleansed by introducing and evacuating the gas several times, and then the discharge figures were taken by the same procedure as in the case of air.

The figures obtained with these gases were, in the main, similar to those obtained with the air-blast, so far as their form was concerned. In the details of the structure, we could however, see some characteristics for each of the gases, especially in the case of hydrogen. The rays were comparatively regular and broad and had fewer side-branches in this case.

(4) The mode of formation of the "splash negative figure"

In order to solve the question of how the "splash negative figures" are formed, it is essential to know the velocity-distribution of the gas-molecules on the photographic plate. Some experiments were undertaken with this object, but the results were generally untrustworthy. The temperature rise was measured by means of a thin constantan-copper thermojunction at many points on the photographic plate, throwing the air-blast upon it as before, and we found that it was greatest between 1 and 1.5 cms. from the nozzle. As the intense fine rays appear mainly in the neighbourhood of the nozzle, we may say that the "splash negative figures" do not depend directly upon the temperature of the gas. But they might depend upon the irregular distribution of gas-pressure produced by the gas-blast.

To test this point still further, a freshly varnished glass plate was used instead of the photographic plate P and the effect of the air-blast on that plate was observed. Fig. 7 in Plate I is a photograph of the surface of the varnished glass plate. In the next place, compressed air (2 atmospheres) which contained traces of grease-vapour, was thrown perpendicularly upon a cleansed glass plate through the jet-tube. (a), (b) and (c) of Fig. 8 in Plate I were obtained when the diameters of the nozzle were 0.6, 0.9 and 1.3 mm. respectively, and the distance between the nozzle and the glass plate was about 1 mm. If the diameter of the nozzle or the value of h was greatly increased, the figure was not clear. The similarity in the character of Fig. 6 and Fig. 7 or 8 in Plate I suggests that the air-blast would produce some irregular air waves on the photographic plate and the electric discharge might mainly take place in the portion where the rarefaction occurred.

If it is so, the side-branches on the "splash negative figure" will also depend upon the irregular distribution of the gas-pressure on the plate or upon the fact that the ions produced are mainly restricted within the narrow rarefaction area. Moreover it seems to be natural to consider that there is a close relation between the formation of the side-branches of the "splash negative figure" and that of the ordinary positive figure.

CHAPTER III

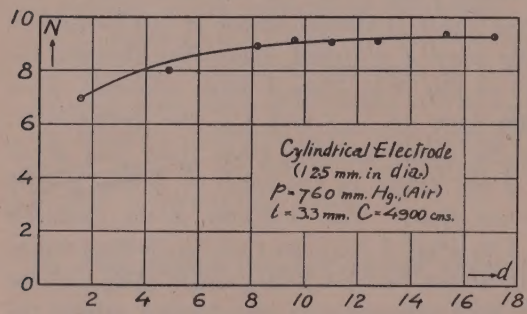
The Side-branches on Positive Stems

In order to explain the mode of the formation of the side-branches on the positive stem, it is important to find the experimental conditions under which their number increases or decreases. As, of course, the counting of the number of the side-branches was somewhat inaccurate, it was desirable to take an average for many stems. The following results are the average values for about 70 stems in each case.

(1) Influence of the thickness of the insulating plate

The relation between the thickness d of the insulating glass plate and the mean number N of the side-branches on one cm. of the stems is shown in Fig. 3.

Fig. 3



For comparatively small values of d, N increases with d. However, when d becomes great, about 1.5 cms. or more, the value of N is nearly independent of it. From this it might be suggested that the formation of the positive side-branches partly depends upon the attraction between the edges of the stem and the earthed plate, or upon the mutual repulsion of the positive ions on the side of stem.

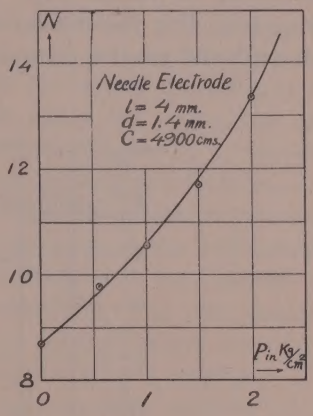
(2) Effect of the pressure of the gas

Prof. P. O. Pedersen[1] has found that N, the number of the side-branches per cm. of the positive stem, is nearly proportional to the pressure P for low pressures. The writer has carried out experiments at pressures higher than 1 atmosphere and found that the value of

1. P. O. Pedersen: Vidensk. Selsk, VIII, **10**, 3, (1929)

N also increases with the pressure. Fig. 4 shows the results: the average number of side-branches per cm. of stems (N) is plotted against the pressure (the reading of the pressure-gauge P Kg/cm^2).

Fig. 4



With $P=2.5$ or over, some intense positive stems with many side-branches appeared and, at the same time, the other stems gradually became feebler and shorter as the pressure increased. Fig. 1 in Plate II, is the positive figure obtained with $P=5$ and $l=6.5$ mm. The following may be a simple explanation of the intense stems. After a sufficient positive charge has accumulated at the discharge-electrode A, a comparatively great number of stems of the discharge-figure starts from the electrode. If, at this stage, the number of the ions in some stems for some reasons becomes greater than in others, these ions will produce more ions by collision and the electric conductivity will increase. As a consequence, a great positive charge is accumulated on the stem, and in the next stage, strong ionization by collision should occur at the edges. Thus intense stems will be produced. As, on the other hand, the electric current in the other stems is gradually reduced with the increase of the electric conductivity of the intense stem, the ionization of air in them will be reduced and cease after a comparatively short time. After that, all the positive charges at the electrode must flow in the intense stems. This tendency may be marked at high pressures, for the high potential at the edges of the stem is necessary for the ionization of air at high pressure. Thus the weak stems will be produced at high pressure.

(3) Effect of spark length

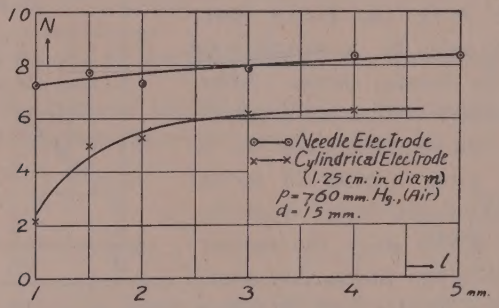
It was found that the mean number of the side-branches per cm. of the positive stems (N) as well as the total number of the stems in the positive figure increased with the length of the spark gap l. Fig. 5 shows some of the experimental results obtained with a condenser (C) whose total capacity was about 4900 cms.

According to J. J. Thomson[1], an electric current i through gas can be represented by an expression of the form

$$V = Ai + Bi^2 \quad \ldots\ldots (1)$$

where A and B are complicated constants and V is the potential difference across the gas. If this is true in our cases, it may be suggested that the number of side-branches increases with the current through the gas for comparatively small spark-lengths.

Fig. 5



(4) Effect of the capacity

Many photographs were taken with a variable air condenser (see C in Fig. 1). The results shew that the number of the side-branches increased very slowly with the capacity from 30 cms. to about 800 cms., but was nearly independent of the capacity for values above 1,000 cms. Next, the writer made some experiments to find the effect of capacities consisting of metal spheres, which were inserted in series with the lead wire to the electrode A. Some of the results are given in Table I.

Table I

Needle electrode,
l=1.5 mm., d=1.6 mm., p=760 mm. Hg.

Radius of sphere in cms.	Average number of side-branches per cm. on the stem
without sphere	7.83
6.3	7.15
12.5	6.65

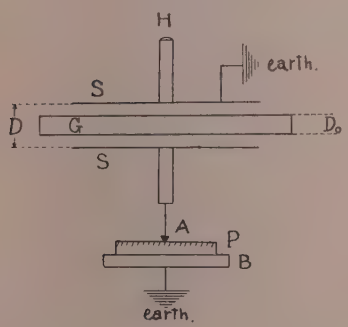
1. J. A. Crowther: "Ions, Electrons and Ionizing Radiation" (Third Edition), 126.

From Table I, it seems to the writer that the number of the side-branches partly depends upon the rate of the rise in the voltage and the potential itself at the discharge-electrode A.

(5) Effect of the rate of the voltage-rise at the electrode

The apparatus used to cause an electric impulse was essentially similar to that shown in Fig. 1 and the impulse was produced by the spark. Consequently, if we wish to know the rate of the voltage-rise at the electrode A, it is necessary to use either the calculation applied by M. Toepler[1] or McEachron's[2] method of inserting a cathode-ray oscillograph into the circuit. But, in the present investigations, our object is to see the qualitative relations between the rate of the voltage-rise at the electrode and the number of the side-branches. For this purpose the writer used a simple apparatus to produce the electric impulse.

Fig. 6



In Fig. 6, SGS consists of a parallel plate condenser. The diameter and the thickness of each circular plate S are 17 cms. and 0.6 mm. respectively, and G is a glass plate, 2 mms. in thickness, which is used to prevent sparking between the plates. A, P and B have the same significance as in Fig. 1.

Now, let us assume that the area of each plate S is so great that the charged conducting plates may be considered as infinite, and that the glass plate with dielectric constant K occupies a thickness D_0 of the space between the plates, whose distance between them is D. Then the capacity C of the condenser SGS is

$$C=\frac{S}{4\pi\left(D-\frac{K-1}{K}D_0\right)} \quad \cdots\cdots(2)$$

If the condenser is charged with electricity Q, and the potential difference between the two plates is V, we get

$$V=\frac{Q}{C} \quad \cdots\cdots(3)$$

1. M. Toepler: Arch. f. Elektrot. **10**, 157, (1921)
2. B. McEachron: A. I. E. E. **45**, 934, (1926)

Let us suppose that the change δV takes place in the potential with an infinitely small change δC in the capacity and that the leakage during an infinitely short time δt is negligible.

Then,

$$\frac{\delta V}{\delta t} = -\frac{Q}{C^2}\frac{\delta C}{\delta t}$$

$$= \frac{4\pi Q}{S}\frac{\delta D}{\delta t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Equation (4) shows that the rate of the voltage-rise at the electrode A is proportional to the rate of increase of the distance between the two plates of the condenser.

In the first place, the condenser SGS was charged positively or negatively by an influence machine and its potential was measured by an electrostatic voltmeter inserted in parallel with two plates of the condenser. If the value of the crest voltage at the electrode A was needed, a needle-gap was inserted in parallel between A and B.

Fig. 3, (a) and (b) in Plate II, shows the negative and the positive figures obtained by slow increase of the distance D, and Fig. 5 (a), (b) in the same plate shows the corresponding figure obtained with the quickest possible increase to the crest-voltage 4.8 KV. In each case, the initial potential difference between the two plates of the condenser was about 3 KV. In the first two figures, all the stems come out from the electrode A, but grow partially round the electrode, and in the positive stems, there are few side-branches. In the latter two figures, the stems grow uniformly round the electrode and the positive stems have a comparatively large number of side-branches, though the lengths of the stems vary.

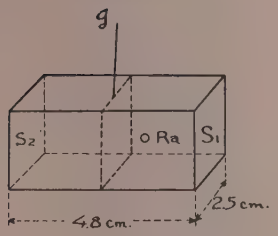
Fig. 4, Plate II is a positive figure obtained by using a coil with an inductance of 18.5×10^{-5} henry, which was inserted in series to the lead wire. The coil used was made of 8 metres of insulated thin copper wire, and was otherwise the same as that described in Fig. 2, Plate II in an earlier paper[1]. In this, it also seems that the decrease in the number of side-branches is partly due to the slow rise of the potential at the electrode.

(6) Influence of free ions

P. O. Pedersen[2] has investigated the influence of initial ionization of the gas within the area of the discharge-figure and concluded that

1. The writer: Mem. Coll. Sci., Kyoto, **13**, 283, (1930)
2. P. O. Pedersen: loc. cit.

Fig. 7



the formation of the regular Lichtenberg figures is independent within very wide limits of the intensity of an existing ionization. The writer has taken many figures with an electrode consisting of two lead boxes with two mica windows S_1 and S_2 as shown in Fig. 7. The β- and γ-rays emitted by the radium placed in one of the boxes passed through one mica window and then fell on the photographic plate placed below the electrode, ionizing the air-molecules. The results of the measurements are summarized in Table II.

Table II

Spark gap l=3 mm. Capacity C=740 cms. Pressure of air=760 mm. Hg.

	Side with Ra.	Side without Ra.
Mean number of positive branches per cm. of the stems	3.4	3.6
Mean length of the positive stems in mm.	14.0	14.4
Mean length of the negative stems in mm.	4.3	4.5

Similar experiments have also been tried with air ionized by the light of an electric spark or a brush-discharge from one electrode of an induction coil. The results were similar to those above; i. e. both the number of the side-branches and the range of the figures were decreased a little by the initial ionization of the air-molecules. This is mainly in agreement with the corresponding result obtained, for the brush discharge, by Prof. Yoshida and Dr. H. Hirata[1].

(7) Influence of fine powders scattered on the photographic plate

In order to see more clearly how side-branches are formed, it is desirable to get much more definite experimental results. P. O. Pedersen[2] took some positive figures in a narrow space between two planes and found that the number of the positive side-branches increased. To investigate whether or not this is due to the increase of the proton-density as stated by Pedersen, similar experiments were made for the

1. U. Yoshida and H. Hirata: Mem. Coll. Sci., Kyoto, **4**, 90, (1919)
2. P. O. Pedersen: loc. cit.

negative figure and the writer found that the negative stem also developed side-branches (see Fig. 6 in Plate II). We can give other examples of this. Fig. 7 in Plate II is a negative figure obtained with a photographic plate on the film of which a second glass plate was placed, a very narrow space being left between them. In the negative figure mentioned above, we can easily see the tree-like negative branches. These results suggest that the negative stem changes to one with side-branches like the positive when the ions on the stem are so restricted that it is impossible for them to diffuse freely in the lateral side of the stem, and that the increase in the number of side-branches in the positive figure in the narrow space is also due to the same cause. If the formation of the side-branches of positive and negative figures depends only upon this—not upon protons—,it should be possible to get positive and negative figures with much more numerous side-branches by using other methods.

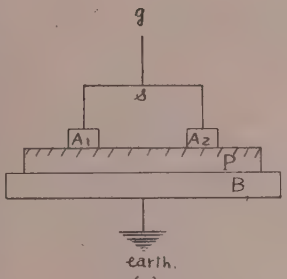
The writer took many discharge-figures with photographic plates, over the films of which well-dried powder (lycopodium, wheat starch, sodium carbonate, calcium sulphate, magnesium oxide or sulphur) was sifted, through a piece of cloth, in a layer so thin as to be hardly visible. In the positive and negative discharge-figures obtained, we could always see many fine stems with numerous side-branches, and this feature in both figures was nearly independent of the ingredients of powder itself. (a) and (b) of Fig. 2 in Plate II are positive discharge-figures obtained with lycopodium powder and without it (compare A_1 and A_2 in Fig. 4, Plate I for the negative figure).

Again it seems to the writer that Pedersen's proton-theory mainly depends upon the fact that the spreading-out velocity of the positive figure is about 2 to 4 times greater than that of the negative. If this is so, it may be of no small significance to see the spreading-out velocity of the figures mentioned above.

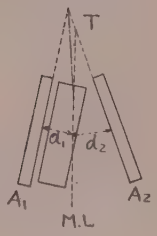
The experimental arrangements used in all the measurements of the spreading-out velocity are schematically shown in Fig. 8, (a); they are similar to those used by Pedersen[1], Przibram[2] and Heymans[3]. In Fig. 8, (a), an electric impulse produced by a spark reaches a point s, and if two branched circuits sA_1 and sA_2 are electrically the same, the impulse divides into two separate waves of equal form, besides

1. P. O. Pedersen: Vidensk. Selsk. I, **11**, 3, (1919)
2. Przibram: Phys. Zs., **21**, 480, (1920)
3. Heymans and Frank: Phys. Rev. **25**, 865, (1925)

the reflected one at s. One of them travels along the wire sA_1 and the other along sA_2, and consequently the meeting line M. L. of two figures, say A_1-figure and A_2-figure, must be at the half-way position between the electrodes A_1 and A_2.



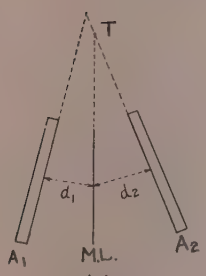
(a)



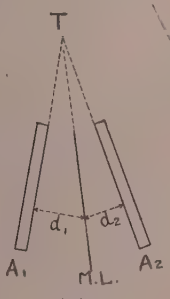
(b)

First of all, many positive discharge-figures were taken with photographic plates, with a glass plate in touch with their sensitive film placed between the electrodes, but rather nearer electrode A_1, as shown in Fig. 8, (b). From this, it was found that the distance d_1 between any point on the meeting line M. L. and the electrode A_1 was always smaller than the distance d_2 between that point and electrode A_2 for the positive figures, but that there was no marked difference for the negative ones, as will be seen from Figs. 8 and 9 in Plate II respectively. This may show that the spreading-out velocity of the positive stem in a narrow space is considerably reduced with the elongation of the positive stem, but that of the negative is not greatly changed.

Fig. 9



(a)



(b)

In the next place, similar experiments were tried with photographic plates, on which lycopodium powder was sifted mainly on the side A_1, though a little may have got on to the side A_2. Fig. 3, and Fig. 4 in Plate I (see also (a) and (b) of Fig. 9) shows the positive and negative figures obtained in this manner. From these figures, it is clear that the distance d_1 is smaller than d_2 in the positive figure, while d_1 is greater than d_2 in the negative, (the first junction of M. L. and electrodes (T) is on A_2 in the positive figures, while it is indefinite in the negative).

These facts described above point to the following conclusions :—

(1) In the positive figure, the spreading-out volocity of the stem is

reduced much more by means of the powder along the stem and this is probably due to the reduction of the field-intensity by the formation of numerous side-branches. (2) In the negative figure, on the other hand, the velocity of the negative stem is observed to be a little greater with the powder and this is perhaps due to the appearance of a number of intense stems (see Fig. 4 in Plate I), on whose edges a strong electric field is formed. (3) The increase in the number of side-branches, both in the figures obtained in confined spaces and in those obtained with the plates on which fine powder had been sifted, may be due to the same cause, but does not depend upon the proton-density. Moreover, it seems to the writer that the smaller spreading-out velocity of the negative stems mainly depends on the weaker field at the edges of the stem, due to greater lateral diffusion of the negative ions or electrons; while the side-branches of the positive figure are probably due to the successive new electrodes with some sharp edges or "thorns", which spring up instantaneously on the positive stems, owing to the smaller mobility of the positive ions.

CHAPTER IV

An Explanation of the Formation of Side-branches in the Positive Figure

About fourteen years ago, Prof. U. Yoshida[1] published a neat theory as to the formation of the discharge-figure and the spark, according to which the formation of the discharge-figures is generally due to ionization by collisions between the gas-molecules and the free electrons. Later, N. E. Dorsey[2] and G. C. Simpson[3] published theories as to the formation of the electric spark, which were, in the main point, similar to Yoshida's. As was stated before, P. O. Pedersen[4] published a proton-theory of the formation of the positive figures. According to his theory, the formation of the side-branches must also be due to the protons. But, recently C. E. Magnusson[5] has investigated the effect of the magnetic field on Lichtenberg figures and con-

1. U. Yoshida: Mem. Coll. Sci., Kyoto Imp. Univ., **2**, 103, (1917)
   U. Yoshida and H. Hirata: loc. cit. (1919)
2. N. E. Dorsey: J. Frank. Inst., April, 485, (1926)
3. G. C. Simpson: Proc. Roy. Soc. A. **111**, 56, (1926)
4. P. O. Pedersen: loc. cit. (1929)
5. C. E. Magnusson: A. I. E. E. **49**, 756, (1930)

cluded, just as Yoshida did, that the electrons are basically the active elements in the formation of the positive as well as the negative figures. Now, it seems to the writer that all the experimental results already described concerning the side-branches on the positive stem are also explained by Yoshida's theory.

Let us consider one of many "thorns" on the circumference of the electrode A. If, at a certain stage, the potential of the electrode reaches a definite value, the electrons existing in front of it will be attracted towards the electrode and acquire sufficient energy to ionize the neutral gas-molecules with which they collide. The positive ions produced in this manner will be forced to move outwards with a comparatively small velocity, but the electrons are attracted towards the electrode and ionize the gas-molecules as before. As a consequence, numerous positive ions are left in front of the "thorn" of the electrode and act as a new positive electrode. As the edges of the stem produced thus may have some "thorns"—for the distribution of the free electrons in the space is irregular and the positive ions have the smaller mobility—the electric field is greater at these sharp points. Consequently, the side-branches will generally grow outwards from these "thorns".

If this hypothesis is tenable the number of side-branches on the positive stem must increase when either the number of "thorns" on the instantaneous electrode or the intensity of the field in its vicinity increases. The former case was supported by the experimental results obtained with photographic plates on which fine powder had been sifted, and the latter by the others: i. e. if a great number of positive ions has accumulated at the instantaneous positive electrodes as a result of an increase in the capacity of the condenser (C), the length of the spark gap (l) or the rate of voltage-rise at the discharge-electrode, then the intensity of the field increases at every "thorn" and consequently the number of side-branches on the stem must also increase.

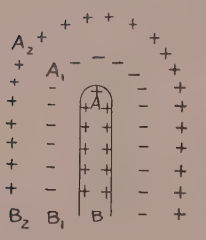
If the capacity between the Lichtenberg gap APB in Fig. 1 is reduced by increasing the thickness of the insulating plate (d), the horizontal intensity of the electric field at the instantaneous electrodes will increase so long as the quantity of the charge and the wave-form remain unchanged. As a result, the number of the side-branches gradually increases with the value of d. As, however, the lateral spreading-out of the positive ions on the "thorn" side increases with

d, the increase in the number of side-branches will stop when d becomes over a certain value, even supposing that the conditions above are unchanged.

If the pressure of the gas increases, the number of main stems decreases and their width is also reduced, because of the high potential necessary for the formation of the stems and also the reduction in the lateral spreading-out of the positive ions. As the reduction in the lateral dissemination of the positive ions in the side portion and the increase in the density of positive ions at the center of the stem may sharpen the "thorns", the average number of side-branches on the stems increases with the pressure.

The problem still left to be explained is the reason why the number of side-branches becomes smaller in the space in which the air-molecules have been previously ionized by the radiations from radioactive substances or by ultra-violet light. Let AB in Fig. 10 be a positive stem, at a certain stage, in the space in question. The ions presented before in the space will, as in the case of the dust figure[1], divide into two layers, one of negative and one of positive ions, as shown by A_1 B_1 and A_2 B_2. According to Prof. U. Yoshida and H. Hirata[2], when an infinite number of electrons of uniform distribution appears in front of the anode, the positive brushes are enormous in number. As it seems to be natural to consider that the same would happen in our case, numerous positive brushes would start from the stem though they are not distinctly impressed on the photographic plate. Such a leakage of electricity causes a reduction of the electric field at the edges of the stem, and both the number of visible side-branches and the length of the positive stem will decrease. This hypothesis may also be applied to the case of the negative stem. If, however, the initial ionization is too strong and the number of negative and positive ions in layers A_1B_1 and A_2B_2 is too great, a somewhat diffuse margin must come in sight at the position A_2B_2[3].

Fig. 10



Now, we must go on to the negative stems. In the case of the negative discharge-figure, the positive ions produced by ionization by

1. The writer: Mem. Coll. Sci., Kyoto, **12**, 217, (1929)
2. U. Yoshida and H. Hirata: loc. cit.
3. The writer: loc. cit.

collisions between the gas-molecules and the electrons are attracted towards the electrode and the negative ions or electrons pushed outwards. The new negative electrode, the negative ions in which may be partly due to the photoelectric effect of the radiation at the negative electrode, as in Thomson's theory[1], will appear at the portion a little distance away from the "thorn" of the electrode. Let AB in Fig. 11 be a negative stem at a certain stage. A′ is a vertex on the outside-layer A′B′ and corresponds to the vertex A on the stem. A crowd of positive ions left in front of the end of the stem in such a manner as shown in the figure will reduce the field-intensity at the edges of the layer A′B′. As, however, the stem AB grows gradually —for the positive ions are neutralized by the negative ions in the stem and numerous negative ions will take their place—the lateral diffusion of the negative ions or electrons in the layer A′B′ will also be increased, especially at the portion near the stem AB. This effect must be all the greater if it is taken into account that the attraction of the earthed metal plate on the negative ions in the stem AB is greater at its central portion than on its side portion. Consequently, we may not find sharp "thorns" on the end of the next electrode A′B′ and there are no side-branches like the positive ones, but the negative stem must gradually broaden. If this is true, then by restricting the lateral diffusion of the electrons or by increasing the number of "thorns" in the successive electrodes, side-branches like those in the positive figure should also be produced in the negative. This hypothesis is supported by the experimental results obtained in a narrow space between glass plates and also by those obtained with powdered plates, and it may also serve to explain the smaller spreading-out velocity of negative figures.

Fig. 11

Finally, the writer wishes to express his sincere thanks to professor U. Yoshida of Kyoto Imperial University for his invaluable suggestions.

The Imperial Japanese Naval College,
Etajima.

1. J. J. Thomson: phil. Mag. **48**, 1, (1924)

Plate I

Fig. 1
l=1 mm. p=70 mm. Hg.

Fig. 2
l=1 mm. p=50 mm. Hg.

(A_1) (A_2)
Fig. 3

(A_1) (A_2)
Fig. 4

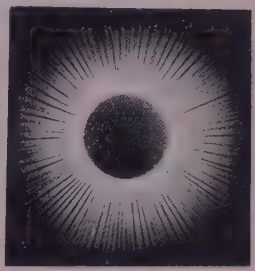


Fig. 5

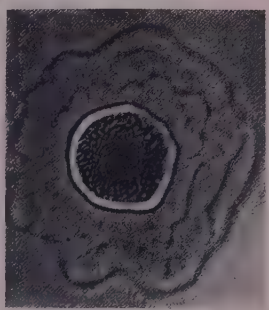
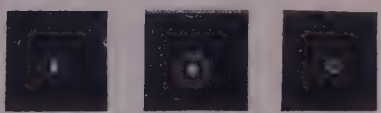


Fig. 7
Refer to Fig. 6

Fig. 6
l=1.3 mm. h=2 mm. p=50 mm. Hg.
diameter of the nozzle=1.3 mm.



(a) (b) (c)
Fig. 8
h=1 mm.
diameter of the nozzle
0.6 0.9 1.3 mm.

Plate II

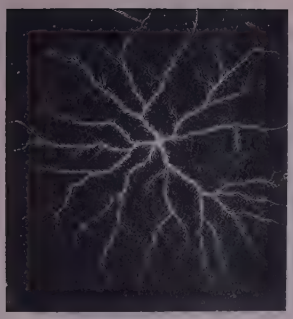
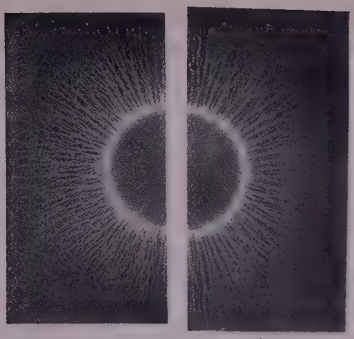


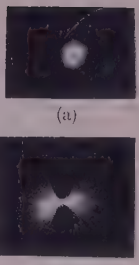
Fig. 1

l=6.5 mm. P=5 $\frac{\text{kg}}{\text{cm}^2}$



(a) (b)

Fig. 2

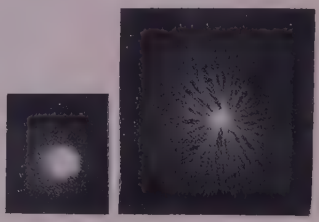


(a) (b)

Fig. 3

Fig. 4

l=1 mm. C=1600 cms. p=140 mm. Hg.
L=1.85×10^{-6} henry



(a) (b)

Fig. 5

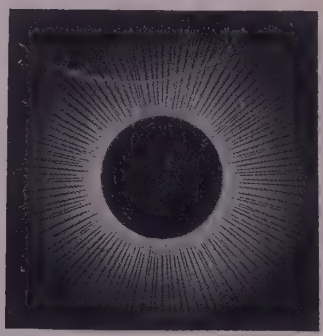


Fig. 6

Fig. 7

Fig. 8

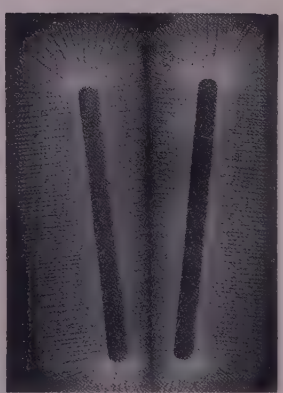


Fig. 9

Study on Sesquiterpenes. I
Sesquiterpene and Sesquiterpene Alcohol from Japanese Camphor Oil *

By

Shigeru Komatsu, Haruki Fujimoto and **Shozo Tanaka**

(Received June 19, 1931)

A high boiling fraction of Japanese camphor oil, named camphor blue oil, has been reported to contain cadinene[1] and bisabolene[2].

Semmler and his co-workers have reported that the sesquiterpene and sesquiterpene alcohol in camphor oil are similar in their chemical nature to camphene. Studying the camphor oil from Formosa, Dr. Kafuku has isolated a sesquiterpene alcohol of tricyclic nature, as ascertained from its physical constants. According to Ono both the sesquiterpene and the sesquiterpene alcohol occurring in Japanese camphor oil gave cadaline when they were oxidized with sulphur. Three sesquiterpene alcohols, primary, secondary and tertiary, of cadaline type are reported to have been isolated from camphor oil by Ruzicka and his pupils.

Sesquiterpene

Researcher	B. p.	d	n_D	$(\alpha)_D$	M. R.
Semmler[3]	$(129°-133°)_8$	0.9015(20/4)	1.5006(20)	+3.0°	66.61
K. Ono[4]	$(140°-141°)_{15}$	0.9025(15/4)	1.5050(15)	+25.3	66.74
Ruzicka[5]	$(127°-128°)_{12}$	0.8876(15/4)	1.4955(15)	—	67.14
„	$(131°-134°)_{12}$	0.8943(14/4)	1.4974(14)	—	66.86
Writers	$(121°-124°)_8$	0.9100(25/4)	1.5046(25)	+17.7	66.45
			M.R. for $C_{15}H_{24}F_2$		66.14

1. Ber. Schimmel Co., 1889, April, 9.
2. Ibid., 1909, October, 24.
3. Ber., **46**, 769.
4. Mem. Coll. Sci., Kyoto Imp. Univ., **8**, 1.
5. Helv., **7**, 264.

* This paper was read before the meeting of the Government Monopoly Bureau, Camphor Department, Taiwan, on June 1929.

Sesquiterpene alcohol

Researcher	B. p.	d	n_D	$(\alpha)_D$	M. R.
Semmler[1]	$(150°-155°)_{16}$	0.9662(20/4)	1.5071(20)	+50.2°	68.39
K. Kafuku[2]	$(130°-133°)_5$	0.9790(18/4)	1.5035(18)	—	66.90
K. Ono[3]	$(160°-163°)_{10}$	0.9595(14/4)	1.5075(14)	+47.3	68.24
„	$(170°-174°)_{10}$	0.9692(„)	1.5084(„)	+64.5	68.39
Ruzicka[4] I	$(156°-158°)_{12}$	0.9568(18/4)	1.5045(18)	+2.2	68.81
„ II	$(160°-162°)_{12}$	0.9720(20/4)	1.5066(20)	−5.2	67.98
„ III	$(156°)_{12}$	0.9665(„)	1.5050(„)	—	68.21
T. Koike[5]	$(156°-159°)_{18}$	0.9654(21/4)	1.5011(21)	+40.9	68.27
„	$(165°-169°)_{18}$	0.9590(21/4)	1.5017(21)	+61.7	68.02
Writers	$(157°-160°)_{12}$	0.9501(25/4)	1.5040(25)	+35.5	68.24
			M. R. for $C_{15}H_{26}OF_1$		68.15

Although these sesquiterpenes and sesquiterpene alcohols isolated by many chemists from camphor oil show similar physical constants, their chemical structures are entirely different according to the investigators, and such difference may be attributed to the difference in the external and internal conditions of the camphor trees from which the oil has been isolated, the geographical conditions in which the trees grow or the age of the tree. It may be more appropriate, however, to attribute it to the difference in the chemical treatment of the oil, by which the structure of the sesquiterpenes will be altered owing to their instability towards chemicals and heat, as we find in the case of a compound having double bonds in the molecule.

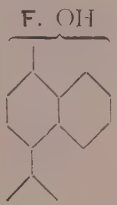
The camphor blue oil which was used in the present study was isolated by distillation from the camphor oil prepared from camphor trees grown in Formosa, and showed the following physical constants: $d_4^{25}=0.937$, $n_D^{25}=1.503$, $(\alpha)_D=+3.7°$ (in alcohol solution). The fraction boiling at $(140°\text{-}180°)_{12}$ was treated with metallic sodium to separate sesquiterpene alcohols as sodium-alcoholate. The sesquiterpene alcohol thus separated from sesquiterpene shows the following physical constants:—

B. p. $(157°\text{-}160°)_{12}$; $d_4^{25}=0.9501$; $n_D^{25}=1.5040$; $(\alpha)_D=+35.5°$;
M. R.=68.24 (M. R. for $C_{15}H_{26}OF_1=68.15$)

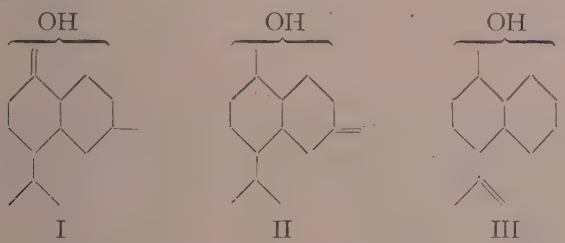
1. Ber., **46**, 770, **47**, 2074.
2. J. Jap. Ind. Chem., **19**, 815.
3. Mem. Coll. Sci. Kyoto Imp. Univ., **8**, 1.
4. Helv., **7**, 264.
5. J. Jap. Ind. Chem., **29**, 215.

When this alcohol was heated with sulphur according to the directions given by Vesterberg, hydrogen sulphide gas was generated, with a hydrocarbon which gave cadaline picrate[1], (M. p. (113°)).

The alcohol, on being treated with phenylisocyanate and acetic anhydride, decomposed into hydrocarbons of the molecular formula $C_{15}H_{24}$, and on reduction with colloidal palladium and hydrogen, with absorption of one mole of hydrogen, yielded a saturated alcohol. The same substance was also obtained by the catalytic reduction of the unsaturated alcohol under high pressure and at high temperature, and thus these facts give rise to the idea that the sesquiterpene alcohol was an unsaturated tertiary alcohol:



To decide the position of the double bond in the molecule, the alcohol was oxidized with ozone, and it was confirmed that formaldehyde, formic acid and keto-alcohol, $C_{14}H_{24}O_2$, occurred in the reaction product. The structure of the alcohol molecule was assigned one of the following three formulae:



I II III

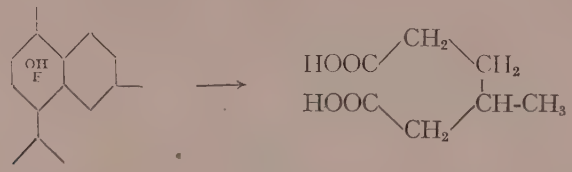
On reduction with metallic sodium and ethyl alcohol, the keto-alcohol yielded an alcohol which gave on dehydration with Japanese acid clay, a hydrocarbon, $C_{14}H_{22}$, and the latter gave acetone as one of products of oxidation with ozone, as was expected from its structure:

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=C_{11}H_{16} \xrightarrow{O_3} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO + C_{11}H_{16}O.$$

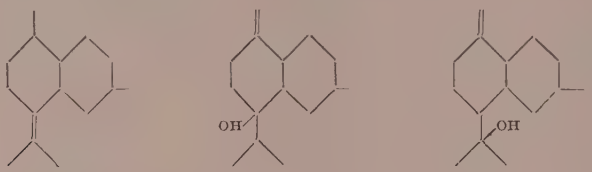
1. Ruzicka u. Mayer: Helv., **4**, 505.

This fact disposes of formula III for the sesquiterpene alcohol.

When the sesquiterpene alcohol was oxidized with alkaline potassium-permanganate solution, oxalic and methyl adipic acids were obtained. The same oxidation products resulted from the hydrocarbon derived from the alcohol by dehydration, and these results are in favour of the view that the double bond and the hydroxyl group of this alcohol should occur in the same ring :—



In order to decide the position of the hydroxyl group in the molecule, the hydrocarbon $C_{15}H_{26}$, which was obtained by the dehydration of the saturated alcohol as mentioned above, was oxidized with ozone, and acetone and ketone $C_{12}H_{20}O$, were obtained in the reaction-products, and formula V or VI (shown below) was assigned to the sesquiterpene alcohol molecule since the hydrocarbon $C_{15}H_{26}$ harmonizes in its chemical behavior with structure IV.



IV V VI

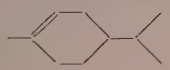
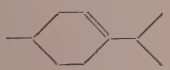
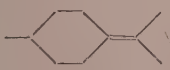
It is a noteworthy fact that the sesquiterpene alcohol yields the following hydrocarbons when various dehydrating agents are used;

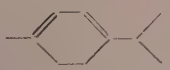
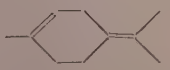
	Dehydrating agent	Molecular formula	B. p.	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.
I	Phenylisocyanate	$C_{15}H_{24}$	$(134°-139°)_{18}$	0.9026	1.4993	+46.6°	66.46
II	Acetic anhydride	$C_{15}H_{24}$	$(136°-142°)_{16}$	0.9058	1.4999	+51.4	66.29
III	Acid clay	$C_{15}H_{24}$	$(131°-134°)_{14}$	0.9060	1.5011	+22.1	66.41
IV	Acid clay	$C_{15}H_{24}$	$(137°-140°)_{14}$	0.9162	1.5066	−23.7	66.29
					M. R. for $C_{15}H_{24}F_2$		66.14

and that these hydrocarbons show different behavior towards hydrochloric gas and mercuric acetate solution, as may be seen from the following table :

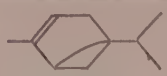
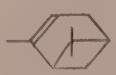
	Dehydrating agent	Hydrochloride	Addition product with mercuric acetate
I	Phenylisocyanate	+	+
II	Acetic anhydride	–	+
III	Acid clay I	–	–
IV	Acid clay II	–	–

Referring to the literature, we noticed that monoterpene hydrocarbons $C_{10}H_{18}$ and $C_{10}H_{16}$ show a close connection between the position of the double bonds in their molecules and their physical constants, as may be seen from the following table.

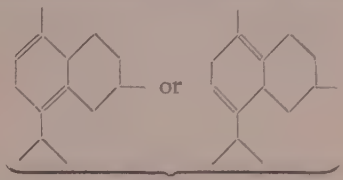
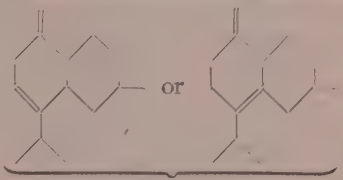
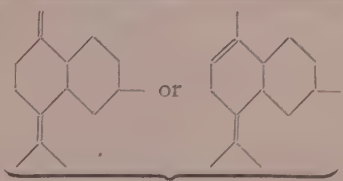
	Structure	B. p.	d_4^{20}	n_D^{20}
Carvomenthene		175°	0.8184	1.4566
Menthene Δ_3		168°	0.8122	1.4524
„ Δ_4		173°	0.8310	1.4647
„ Δ_8		170°	0.8104	1.4566

Monocyclic terpenes	Structure	B. p.	d_4^{20}	n_D^{20}
α-Terpinene		175°	0.8453	1.4858
α-Phellandrene		175°	0.8440	1.4732
β-Phellandrene		172°	0.8520	1.4788
Terpinolene		184°	0.8540	1.4840

Monocyclic terpenes	Structure	B. p.	d_4^{20}	n_D^{20}
Crithmene		179°	0.8658	1.4806
Limonene		175°	0.8426	1.4699
Isolimonene		172°	0.8370	1.4704
Menthadien 3,8		184°	0.8574	1.4943

Bicyclic terpenes	Structure	B. p.	d_4^{20}	n_D^{20}
Thujene		152°	0.8275	1.4504
Sabinene		163°	0.8481	1.4673
Pinene		155°	0.8542	1.4634
Nopinene		162°	0.8660	1.4724

Hydrocarbons which have a double bond in the side chain, especially between carbons 4 and 8, show much higher values for their physical constants than the calculated value; a similar fact was noticed in the case of the hydrocarbons having a conjugate double bond. If the rule as to the connection between the position of the double bond and the physical constants of monoterpenes is taken into consideration, the following structures for the sesquiterpenes produced from sesquiterpene alcohol by dehydration may be suggested from the study of their physical constants :—

	Dehydrating agent	Structure
I	Phenylisocyanate	 VII
II	Acetic anhydride	 VIII
III & IV	Acid clay	 IX

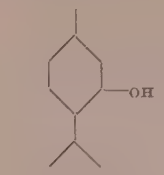
And the fact that four hydrocarbons when oxidized with ozone, yield the reaction products indicated in the following table, gives strong support to the structures of the hydrocarbons shown above.

	Dehydrating agent	Reaction Product	
		Volatile matter	Nonvolatile matter
I	Phenylisocyanate	nul	–
II	Acetic anhydride	HCHO, HCOOH	$C_{14}H_{22}O_4$
III	Acid clay I	$(CH_3)_2CO$	$C_{12}H_{18}O_4$
IV	Acid clay II	$(CH_3)_2CO$	$C_{11}H_{18}O_3$

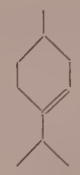
All these reactions are in favour of structure (V) for the alcohol so far studied.

It was noticed that the chemical structure of terpene hydrocarbons

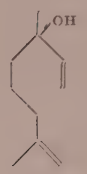
shows a close relationship to that of the terpene alcohols which occur side by side in the same essential oil, such as menthene and menthol in peppermint oil, limonene and linalool in citrus oils and cadinene and cadinol in galbaumoil.



Menthol

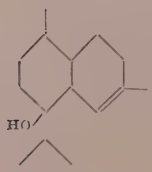


Menthene

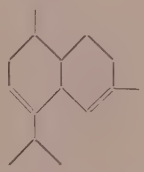


Linalool

Limonene



α-Cadinol



α-Cadinene

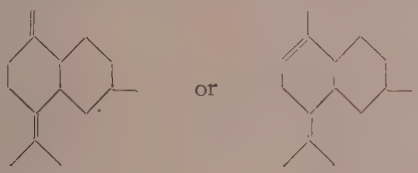
Such a structural relationship as holds between terpenes and terpene alcohols was assumed to exist between the sesquiterpenes and sesquiterpene alcohol in Japanese camphor blue oil, and the writers started on the study of the structure of the sesquiterpene in camphor oil from this assumption.

The hydrocarbons which were separated from the sesquiterpene alcohol, contained 16 % of the blue oil and were divided by fractional distillation into the following three parts :—

Fraction	B. p.	Molecular formula	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.
1	(119°–121°)$_3$	$C_{15}H_{24}$	0.9128	1.5046	+16.2°	66.25
2	(121°–124°)$_8$	$C_{15}H_{24}$	0.9100	1.5046	+17.7	66.45
3	(124°–127°)$_9$	$C_{15}H_{24}$	0.9162	1.5055	+17.3	66.71
				M. R. for $C_{15}H_{24}F_2$		66.14

The three fractions gave neither solid hydrochloride, nitrosate nor nitrosochloride and were therefore supposed to be composed of isomeric hydrocarbons of formula I or II; this assumption was partly supported by the fact that the hydrocarbons produced from the sesquiterpene alcohol by dehydration with acid clay showed similar physical and chemical properties to those of the sesquiterpenes.

	$C_{15}H_{24}$ (natural)	$C_{15}H_{24}$ (from $C_{15}H_{26}O$)
B. p.	$(121°-124°)_8$	$(131°-134°)_{14}$
d_4^{25}	0.9100	0.9060
n_D^{25}	1.5047	1.5011
$(\alpha)_D$	$+17.7°$	$+22.1°$
M. R.	66.45	66.41
Hydrochloride	—	—



(I) or (II)

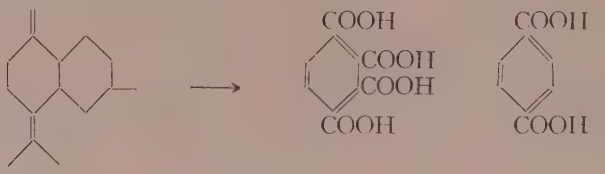
This view of the structure of the sesquiterpenes is favoured by the fact that they give the same tetrabromide,[1] and also cadaline results from oxidation with sulphur.

Fraction	Br_2 added	Br_2 % for $C_{15}H_{24}Br_4$
1	57.25	
2	57.89	61.05
3	58.28	

The double bonds in the molecule of the sesquiterpene being unreducible by means of metallic sodium and amyl alcohol[2], were regarded as not existing in a conjugate system but rather, from reference to the abnormality of their physical constants as being situated in side chains as shown in (III). The oxidation of the hydrocarbon with potassium permanganate or with manganese dioxide[3] and sulphuric

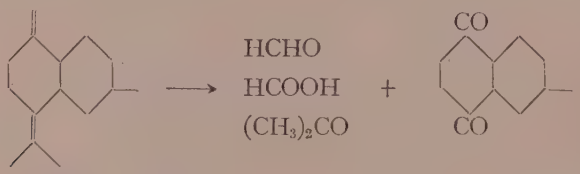
1. Allen: Analyst, **6**, 177; Levallois: C. R., **99**, 977.
2. Semmler: Ber., **56**, 1033.
3. Ruzicka u. Stoll: Helv., **7**, 84.

acid proves that the writers' assumption as to the structure is accurate, isophthalic acid being obtained in the former case and prehnitic acid in the latter.

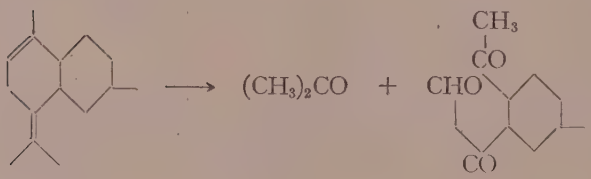


III

The fact that formaldehyde, formic acid, acetone and acetic acid were obtained as volatile reaction products from the sesquiterpene by oxidation with ozone on the one hand, and on the other, diketone $C_{11}H_{14}O_2$ and an aldehyde in a nonvolatile reaction product, is in favour

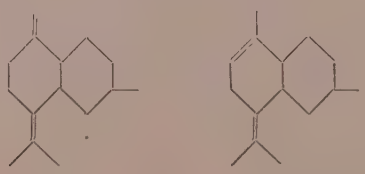


XIII



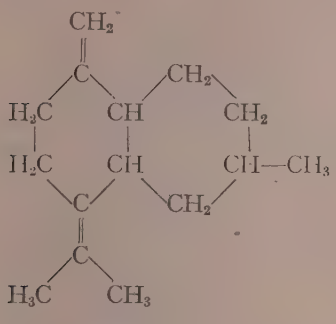
XIV

of the view that the sesquiterpene obtained from the camphor blue oil must be a mixture of two hydrocarbons represented by the following structures, IV and V.

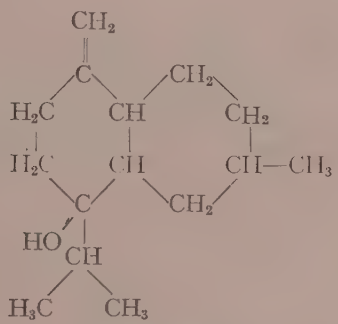


IV V

The compound which corresponds to formula V was supposed to be derived from the other (IV) by an intermolecular change during the treatment of the oil, and this assumption was proved to be partly true, as the sesquiterpene no longer gives volatile reaction products such as acetone on ozone-oxidation after repeated distillation with metallic sodium, owing to the dislocation of the double bond in the molecule. The sesquiterpene and sesquiterpene alcohol isolated by the writers from Japanese camphor oil were thus assertained to have the following chemical constitutions :—



Sesquiterpene



Sesquiterpene alcohol

EXPERIMENTAL PART

(A) Sesquiterpene Alcohol

I. Separation of sesquiterpene alcohol

The camphor blue oil obtained from camphor trees grown in Formosa was fractionated into the following 3 parts :

Fraction	B. p.	Yield
1	($-140°)_{12}$	40%
2	(140°–180°) „	50%
3	(180°–) „	10%

500 gms. of fraction (2) were heated at 50°-60° under a pressure of 12-15 m.m. for 50 hours with 35 gms. of metallic sodium, and the

hydrocarbons occurring in the oil distilled off. The residue which consisted mostly of the sodium-salt of sesquiterpene alcohol was decomposed with ether containing water to get the alcohol in a free state and the yield of the alcohol and the hydrocarbon was as follows :

	Yield	
	gms.	%
Hydrocarbon	210	23
Alcohol	200	22
Resinous matter	60	5

The alcohol separated from the hydrocarbon was distilled under reduced pressure and 5 fractions with the following properties were obtained :—

Fraction	B. p.	Yield	d_4^{25}	n_D^{25}	$(\alpha)_D$
1	($-157^\circ)_{12}$	2.2%	—	1.5030	$+20.6^\circ$
2	$(157^\circ-160^\circ)_{12}$	6.2	0.9501	1.5040	$+35.5$
3	$(160^\circ-166^\circ)_{12}$	0.9	—	1.5048	$+32.4$
4	$(166^\circ-170^\circ)_{12}$	2.1	0.9450	1.5044	$+29.2$
5	$(170^\circ-175^\circ)_{12}$	2.2	—	1.5044	$+25.6$

Fraction (2) was found to consist of sesquiterpene alcohol from its physical constants and also from elementary analysis :

B. p. $(157^\circ\text{-}160^\circ)_{12}$; $d_4^{25}=0.9501$; $n_D^{25}=1.5040$; $(\alpha)_D=+35.5^\circ$;

M. R. 68.24 (M. R. for $C_{15}H_{25}OF_1=68.15$)

	Calc. for $C_{15}H_{26}O$	Found
Carbon	81.08	80.8
Hydrogen	11.71	12.0

II. Oxidation of sesquiterpene alcohol with sulphur

25 gms. of the sesquiterpene alcohol were heated with 35 gms. of sulphur at $180^\circ\text{-}230^\circ$ for 12 hours and the reaction product was distilled on metallic sodium. The hydrocarbon thus obtained showed the following physical constants :

B. p. $(145^{\circ}\text{-}160^{\circ})_{22}$; $d_4^{25}=0.9561$; $n_D^{25}=1.5408$;
M. R. 65.10 (M. R. for $C_{15}H_{13}F_5$ 64.72)
This substance yields orange coloured needles of cadaline picrate (M. p. 113°).

III. Reduction of sesquiterpene alcohol

(*a*) *Reduction of the Alcohol with Colloidal Palladium and Hydrogen*

10 gms. of the sesquiterpene alcohol were treated in 50 gms. of glacial acetic acid solution with palladium colloid (which contained 0.025 gm. of Pd) and hydrogen at 40-50° under 2 atmospheric pressures for 16 hours and the amount of hydrogen absorbed indicated that it contained one double bond in the molecule. The reaction product was distilled under reduced pressure and a saturated alcohol having the following constants was obtained:—
B. p. $(145^{\circ}\text{-}150^{\circ})_{12}$; $d_4^{25}=0.9388$; $n_D^{25}=1.4901$; $(\alpha)_D=+7.5^{\circ}$;
M. R. = 69.10 (M. R. for $C_{15}H_{28}O$ = 68.60)

	Calc. for $C_{15}H_{28}O$	Found
Carbon	80.29	80.2
Hydrogen	12.58	12.4

(*b*) *Reduction of the Alcohol with Reduced Nickel and Hydrogen under High Pressure and at High Temperature*

50 gms. of the sesquiterpene alcohol were heated in an autoclave with 5 gms. of reduced nickel and hydrogen at 150°-160° under 80 atmospheric pressures and the fall in the hydrogen pressure was 35 atmospheric pressures. The product was fractionated into the following two parts:

Fraction	B. p.	Yield	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.
1	$(160^{\circ}-164^{\circ})_{19}$	16 gms.	0.9303	1.4897	+16.6°	69.64
2	$(164^{\circ}-168^{\circ})_{19}$	16 „	0.9414	1.4943	+20.7	69.23
				M. R. for $C_{15}H_{28}O$		68.60

The saturated alcohols produced by two reducing methods were dehydrated separately by heating with acid clay, and the hydrocarbons (A & B) generated were found to be the same by reference to their physical constants :—

	Molecular formula	B. p.	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.
A	$C_{15}H_{26}$	$(123°-125°)_{12}$	0.8877	1.4887	−12.2°	67.06
B	$C_{15}H_{26}$	$(138°-140°)_{20}$	0.8898	1.4870	−11.2	67.29
					M. R. for $C_{15}H_{26}F_1$	66.60

IV. Oxidation of the sesquiterpene alcohol with ozone

Ozonized air was passed into a 20 % carbon tetrachloride solution of the sesquiterpene alcohol and the solvent distilled off under diminished pressure, and an ozonide remaining in the flask was decomposed with water. The aqueous solution separated from an oily reaction product showed (1) Lieben's reaction[1] for iodoform, (2) red colouration of a fuchsin solution decoloured by SO_2, (3) reduction of a silver ammoniacal solution, (4) red colouration of a solution containing a few drops of 1 % phenol solution with conc. sulphuric acid.

These reactions indicate the presence of formaldehyde and formic acid in the aqueous solution.

The oily reaction product was washed with dilute caustic soda solution and analysed after being dried in a vacuum desiccator.

	Calc. for $C_{14}H_{24}O_2$	Found		
		I	II	III
Carbon	74.93	74.6	74.3	74.7
Hydrogen	10.79	10.5	10.6	10.3

It was reduced with metallic sodium and ethyl alcohol to an alcohol which was then subjected to steam distillation. The alcohol after being purified showed the following properties :—

B. p. $(137°\text{-}140°)_5$; $d_4^{25}=0.9735$; $n_D^{25}=1.5029$; M. R. $=63.82$;
(M. R. for $C_{14}H_{25}O$ 63.98).

1. Rosenthaler: Der Nachweis organischer Verbindungen. S. 161.

	Calc. for $C_{14}H_{26}O$	Found		
		I	II	III
Carbon	79.92	79.7	79.7	79.8
Hydrogen	11.46	11.5	11.5	11.5

When acted upon by phenylisocyanate or Japanese acid clay, the alcohol gives a hydrocarbon, and on being heated with phthalic anhydride at 120°, an acidphthalate.

The hydrocarbon $C_{14}H_{24}$ generated from the alcohol by treatment with the acid clay showed the following physical constants :—

B. p. $(143°\text{-}145°)_{30}$; $d_4^{25}=0.9321$; $n_D^{25}=1.5058$; M. R.$=61.24$;
(M. R. for $C_{14}H_{24}F_1=61.99$).

The analytical results were :—

	Calc. for $C_{14}H_{24}$	Found
Carbon	87.43	87.1
Hydrogen	12.57	12.4

Oxidation of the hydrocarbon with ozone was tried and the reaction product consisted of acetone and a carbonyl compound which gave on analysis the following results, and also a semicarbazone, M. p. (162°-170°).

	Calc. for $C_{14}H_{24}O_3$	Found
Carbon	69.94	70.7
Hydrogen	10.08	10.0

V. Oxidation of sesquiterpene alcohol with potassium permanganate

β-Methyl Adipic Acid

To a mixture of 1 part of the sesquiterpene alcohol and 10 parts of 10% caustic soda solution, powdered potassium permanganate was added slowly at 60°. The solution, separated from manganese-dioxide by filtration, was acidified with dilute hydrochloric acid, evaporated to dryness and treated with absolute alcohol to extract an acid formed by the oxidation. This was isolated in a syrupy form which

was changed to white crystals on standing in a vacuum desiccator, melting at about 80° with decomposition. Into an etherial solution of this acidic compound dry ammonia gas was passed, and the ammonium salt was converted into a silver salt which was analysed after drying in a vacuum desiccator.

	Calc. for $C_7H_{10}O_4Ag_2$	Found	
		I	II
Carbon	22.49	20.9	19.9
Hydrogen	2.67	2.4	2.5
Silver	57.73	58.4	57.1

The physical and chemical properties of the acid, and also the analytical results agree with those of β-methyl adipic acid.

VI. Oxidation of the hydrocarbon $C_{15}H_{26}$ derived from the saturated alcohol $C_{15}H_{28}O$

The hydrocarbon $C_{15}H_{26}$, which was produced by dehydration of the saturated alcohol as mentioned above, was oxidized with ozone in carbon tetrachloride solution, and an ozonized substance was decomposed with hot water. The aqueous solution of this was proved to contain acetone by ;

(1) Lieben's iodoform reaction, (2) the reaction to Fehling's solution, (3) the colouration of fuchsin solution decoloured by SO_2, (4) giving a ruby-red colour with an alkaline solution of sodium nitroprusside, (5) Frommer-Emilowicz's reaction[1], (6) giving dibenzalacetone, M. p. (110°).

The other reaction product, which was insoluble in water, was reduced with metallic sodium and ethyl alcohol, and the reduced substance gave the following constants, corresponding to alcohol $C_{12}H_{22}O$.

B. p. $(120°\text{-}130°)_4$; $d_4^{25}=0.9163$; $n_D^{25}=1.4789$; $(\alpha)_D=-7.2°$;
M. R. = 56.38 (M. R. for $C_{12}H_{22}O=54.74$) :

	Calc. for $C_{12}H_{22}O$	Found	
		I	II
Carbon	79.04	79.0	79.3
Hydrogen	12.17	12.3	12.0

1. Rosenthaler: Der Nachweis organischer Verbindungen. S. 161.

The alcohol thus formed gave a phenyl urethane derivative and also an acid phthalate when heated with phthalic anhydride at 180° for 8 hours, and these reactions agree with those of a secondary alcohol. On distillation with acid clay, it yielded a hydrocarbon with the constants.

B. p. $(145°\text{-}155°)_{25}$; $d_4^{25}=0.8934$; $n_D^{25}=1.4894$; M. R.$=53.67$;
(M. R. for $C_{12}H_{20}F_1=52.75$)

VII. Dehydration of sesquiterpene alcohol

(*a*) *Dehydration of Sesquiterpene Alcohol with Phenylisocyanate*

When the sesquiterpene alcohol was heated in a sand bath with an equal quantity of phenylisocyanate, the reaction took place with the evolution of carbon dioxide, and the chief product was a hydrocarbon which was distilled with metallic sodium under reduced pressure. The main fraction was found to consist of hydrocarbon $C_{15}H_{24}$, by the determination of its density and index of refraction and also by the analysis :—

B. p. $(134°\text{-}139°)_{18}$; $d_4^{25}=0.9026$; $n_D^{25}=1.4993$; $(\alpha)_D=+46.6°$;
M. R.$=66.46$ (M. R. for $C_{15}H_{24}F_2=66.14$).

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	87.8
Hydrogen	11.85	12.1

It yields dihydrochloride, (M. p. 191°) when treated by the usual method, and also an amorphous white mercury compound on shaking with a mercury acetate solution. By the oxidation of this hydrocarbon with ozone, an oily substance containing a carbonyl group in the molecule was isolated, which gave a semicarbazone, (M. p. 90°-93°).

(*b*) *Dehydration of Sesquiterpene Alcohol with Acetic Anhydride*

When a mixture of the alcohol and acetic anhydride was heated in a sealed tube at 150°-160° for 6 hours, a hydrocarbon of the following nature was obtained :—

B. p. $(136°\text{-}142°)_{16}$; $d_4^{25}=0.9058$; $n_D^{25}=1.4999$; $(\alpha)_D=+51.4°$;
M. R.$=66.29$ (M. R. for $C_{15}H_{24}F_2=66.14$)

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	87.9
Hydrogen	11.85	12.1

This substance gave a white mercury compound when acted on by mercury acetate solution but not any solid hydrochloride. On oxidation with ozone, it yielded formaldehyde, formic acid and a carbonyl compound, and the latter substance gave a semicarbazone showing M. p. 63°-65° and the following analytical results :—

	Calc. for $C_{14}H_{22}O_4$	Found		
		I	II	III
Carbon	66.10	65.7	66.1	66.5
Hydrogen	8.60	8.9	9.1	9.1

(*c*) *Dehydration of Sesquiterpene Alcohol with Japanese Acid Clay.*

The sesquiterpene alcohol was distilled with the acid clay and the product was divided into two portions after being purified by distilling on metallic sodium.

Fraction 1.

B. p. $(131°\text{-}134°)_{14}$; $d_4^{25}=0.9060$; $n_D^{25}=1.5011$; $(\alpha)_D=+22.1°$;
M. R.=66.41 (M. R. for $C_{15}H_{24}F_2=66.14$)

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	88.0
Hydrogen	11.85	12.0

Fraction 2.

B. p. $(137°\text{-}140°)_{14}$; $d_4^{25}=0.9162$; $n_D^{25}=1.5066$; $(\alpha)_D=-23.7°$;
M. R.=66.29 (M. R. for $C_{15}H_{24}F_2=66.14$)

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	87.9
Hydrogen	11.85	11.5

Neither fraction gave solid hydrochloride with hydrochloric acid nor a mercury derivative with mercury acetate. On oxidation with

ozone, fraction (1) yielded a large quantity of acetone and a carbonyl-compound, and the latter, which gave a semicarbazone with M. p. 55°-57°, was analysed.

	Calc. for $C_{12}H_{18}O_4$	Found	
		I	II
Carbon	63.70	62.2	62.1
Hydrogen	7.90	8.2	8.5

On oxidation with ozone fraction (2) gave acetone and a carbonyl compound $C_{11}H_{18}O_3$, which showed the following analytical results :—

	Calc. for $C_{11}H_{18}O_3$	Found	
		I	II
Carbon	66.70	65.6	66.2
Hydrogen	9.10	8.9	9.0

B. Sesquiterpene

I. Isolation of sesquiterpene

3 kgms. of the camphor blue oil were treated with 30 gms. of sodamide at 50° under diminished pressure for 60 hours, and after the evolution of ammonia had ceased, the reaction product was distilled under reduced pressure, 1.1 kgms. of distillate being obtained.

It was fractionated several times on metallic sodium and the following 5 portions were obtained.

Fraction	B. p.	Yield	
		gms.	%
1	(50°—87°)$_3$	150	5.0
2	(87°—98°)„	165	5.5
3	(98°—112°)„	360	12.0
4	(112°—125°)„	135	4.5
5	(125°—)„	275	9.1

Fraction (3) was divided into the following 3 fractions and the physical constants of each were determined. The analytical results agree with those for sesquiterpene, $C_{15}H_{24}$ (C=88.15 ; H=11.85).

Fraction	B. p.	Yield	d_4^{25}	n_D^{25}	$(\alpha)_D$	M. R.	C	H
1	(119°–121°)$_8$	92 gms.	0.9128	1.5046	+16.2°	66.25	87.7	11.8
2	(121°–124°)$_{,,}$	134	0.9100	1.5046	+17.7	66.45	87.9	11.8
3	(124°–127°)$_{,,}$	83	0.9162	1.5055	+17.3	66.72	87.8	11.9
				M. R. for $C_{15}H_{24}F_2$		66.14		

Preparation of Hydrochloride

In an etherial solution of the three fractions, hydrochloric gas was passed until the solution was saturated with the gas. It was then left to stand for a long time in an ice box, but no solid hydrochloride was noticed to form in the solution.

Preparation of Nitrosate

A mixture of 5 gms. of each fraction, 15 gms. of glacial acetic acid and 5 gms. of amyl nitrite, was cooled with a cooling mixture of ice and salt, and 5 gms. of conc. nitric acid were added slowly to the solution and the mixture was kept in a refrigerator for a few days but no crystalline substance appeared from the solution.

Preparation of Nitrosochloride

5 gms. of each hydrocarbon dissolved in 15 gms. of glacial acetic acid, and 5 gms. of amyl nitrite were mixed under cooling, and absolute alcohol saturated with hydrochloric gas was added slowly. No solid substance separated out from the solution when it was kept in a cold place for a long time.

II. Addition of bromine to the sesquiterpene

In accordance with Allen's method, a carbon tetrachloride solution of the sesquiterpene was mixed with a known quantity of 1/3 N carbon tetrachloride solution of bromine, and the mixture was left to stand for 18 hours, and free and combined bromines were determined as usual. The bromine required for the double bonds in the compound was calculated, with the following results:—

Fraction	Substance	Br_2 absorbed	Br_2 substituted	Br_2 added	% of Br_2 (add. product)
1	0.4242 gm.	0.8646 gm.	0.2964 gm.	0.5682 gm.	57.25
2	0.4292	0.8919	0.3019	0.5900	57.89
3	0.6566	1.2367	0.3193	0.9174	58.29
				Br_2 Calc. for $C_{15}H_{24}Br_4$	61.05

These results show that these three fractions consist of the same sesquiterpene, of a bicyclic nature, having two double bonds in the molecule.

III. Oxidation of sesquiterpene with sulphur

30 gms. of the sesquiterpene were heated with 15 gms. of sulphur at 180°-200° for 10 hours, and the reaction product, purified by distillation on metallic sodium, showed the following constants :—

B. p. $(120°\text{-}135°)_9$; $d_4^{25}=0.9573$; $n_D^{25}=1.5419$; M. R.=65.08;
(M. R. for $C_{15}H_{18}F_5=64.72$)

This substance gave a picrate of orange coloured needles which were identical in M. p. (114°) with cadaline picrate.

IV. Reduction of the sesquiterpene with metallic sodium and amyl alcohol

An amyl alcohol solution of 20 gms. of the sesquiterpene was heated to boiling and 15 gms. of sodium were added to the solution. The reduced sesquiterpene was purified on metallic sodium and showed the following constants :—

B. p. $(100°\text{-}110°)_4$; $d_4^{25}=0.9189$; $n_D^{25}=1.4981$; $(\alpha)_D=+12.7°$;
M. R.=65.73 (M. R. for $C_{15}H_{24}F_2=66.14$)

	Calc. for $C_{15}H_{24}$	Found
Carbon	88.15	87.9
Hydrogen	11.85	11.6

These results show that two double bonds in the sesquiterpene remained without entering into any reaction with amyl alcohol and metallic sodium.

V. Oxidation of the sesquiterpene with potassium permanganate

20 gms. of the sesquiterpene were dissolved in a mixture of 200 gms. of acetone and 50 gms. of water, and 22 gms. of powdered potassium permanganate were added gradually under vigorous agitation at the room temperature. This was filtered from manganese dioxide, and acetone was distilled off under reduced pressure, and an oily neutral substance which separated out on the surface of the solution

was extracted with ether. The aqueous solution separated from the oily matter, gave 1.3 gms. of a white crystalline acidic substance together with oxalic acid on acidifing with hydrochloric acid. This acidic substance was easily separated from the oxalic acid by transforming into their calcium salts. The free acid, purified by sublimation, melted at 228° with decomposition and gave on micro-analysis the following results :—

	Calc. for $C_8H_6O_4$	Found	
		I	II
Carbon	57.80	57.3	57.3
Hydrogen	3.60	3.3	3.7

The physical and chemical properties of this substance were identical with those of isophthalic acid.

VI. Oxidation of the sesquiterpene with manganese dioxide and sulphuric acid

30 gms. of the sesquiterpene were oxidized in a boiling state with 500 gms. of conc. sulphuric acid, 600 c. c. of water and 37 gms. of manganese dioxide.

An aqueous solution separated from unchanged manganese dioxide was treated with ether to extract an acidic substance which was formed from the hydrocarbon by the oxidation ; this was isolated in a syrupy form. It was converted into a silver salt by means of alcoholic silver nitrate solution, and by being transformed into the methyl ester was identified as prehnitic acid. The dimethyl ester purified from its alcohol solution melted at 172° and gave the following analytical results :

	Calc. for $C_{12}H_{10}O_6$	Found
Carbon	51.10	52.2
Hydrogen	3.50	3.6

VII. Oxidation of the sesquiterpene with ozone

The sesquiterpene dissolved in chloroform was oxidized with ozone by the usual method, and after the completion of the reaction the solvent was distilled off under reduced pressure and a white syrupy ozonide, thus obtained, was decomposed with boiling water.

An aqueous solution separated from an oily substance formed from the ozonide was proved to contain formaldehyde by;

(1) the reduction of an ammoniacal silver oxide,

(2) reduction of Fehling's solution,

(3) the colour reaction to a sodium nitroprusside solution and phenylhydrazine hydrochloride solution,

(4) the formation of the phenylhydrazone, M. p. 168°.

The occurrence of formic acid and acetic acid in the solution was confirmed by the fact that it formed white silver salts with silver nitrate solution and also by;

(1) the colour reaction to ferric chloride solution,

(2) formation of a white precipitate with mercurous acetate,

(3) formation of the ethyl ester with ethyl alcohol and conc. sulphuric acid.

The presence of acetone in the solution was also confirmed by;

(1) a purple-red colouration with sodium nitroprusside and ammonium sulphate,

(2) a red colouration with sodium nitroprusside and caustic soda solution,

(3) Lieben's iodoform reaction,

(4) a dark red colouration with salicylaldehyde and caustic soda,

(5) Dibenzalacetone, M. p. 110° obtained by treating it with benzaldehyde and a large amount of alcoholic potash.

The oily reaction product separated from the acidic solution was subjected to steam distillation and the volatile substance thus obtained was fractionated under reduced pressure. The main fraction boiling at $(100°\text{-}110°)_4$, consisted of a ketone with the formula $C_{11}H_{22}O_2$, which gave a semicarbazone with M. p. 219° and the analytical results.

N = 29.1; theory requires N = 31.2 for $C_{11}H_{22}O_2N_6$.

A resinous substance formed from the oily reaction substance by steam distillation showed an intense reducing action and on oxidation with ammoniacal silver oxide gave a carboxylic acid, the structure of which could not be decided owing to the small amount of the substance.

In conclusion, the writers wish to express their hearty thanks to the Government Monopoly Bureau, Camphor Department, Taiwan for a research grant.

April, 1930.

Laboratory of Organic- & Bio-Chemistry.

Stereochemical Studies on Hydronaphthalene and Its Derivatives

By

Sakuziro Kimura

(Received June 19, 1931)

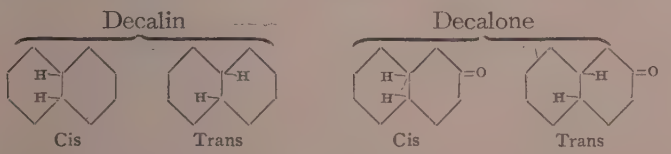
Part I

Catalytic Reduction of β-Naphthol under High Temperature and High Pressure

The stereochemistry of hydronaphthalenes and their derivatives has already been studied by many investigators, and cis and trans isomers with the following physical constants have been noticed to exist in decahydronaphthalene (decalin) and decalone[1].

	B. p.	d_4^{20}	n_D^{20}
Cis-Decalin	$(193-193.5)_{760}$	0.8942	1.4795
Trans-Decalin	$(187-188)_{760}$	0.8756	1.4706
Cis-β-Decalone	$(244)_{744}$	1.0029	1.49218
Trans-β-Decalone	$(238)_{746}$	0.9760	0.48215

It is customary to explain the occurrence of these stereoisomers in the hydronaphthalene derivatives by assuming the bicyclic hexamethylene structure for hydronaphthalene.



1. H. Leroux, Compt. rend., **141**, 953 (1905); W. Ipatiew, Ber., **40**, 1287 (1907); N. Zelinsky, Ber., **56**, 1723 (1923); **57**, 2062 (1924); **58**, 1292 (1925); R. Willstätter u. F. Seitz, Ber., **57**, 683 (1924); F. Eisenlohr u. R. Polenski, Ber., **57**, 1639 (1924); W. Hückel, Chem. Zentr., III, 766 (1923); Ber., **58**, 1449 (1925); Ann., **441**, 42 (1925).

It has also been reported that four isomers with the following constants[1] exist in β-decalol. (decahydro-β-naphthol).

		B. p. 746 mm.	M. p.
(I)	Cis-cis-β-Decalol	242–243°	105°
(II)	Cis-trans-β-Decalol	242.5–243°	17°
(III)	Trans-cis-β-Decalol	236°	75°
(IV)	Trans-trans-β-Decalol	230–231°	53°

The configurations of these decalols were confirmed by oxidizing with chromic acid into decalone; both the decalols with M. p. 105° and that with M. p. 17° give cis decalone, and trans-decalone is equally derived the two decalols with M. p. 75° and 53°. In decalone, which has two asymmetrical carbon atoms in the molecule, four optical

Cis-β-Decalone		Trans-β-Decalone	
(I)	(II)	(III)	(IV)
+	−	+	−
+	−	−	+

isomers are possible and in the same way eight optical isomers may be expected to exist in decahydronaphthol. The isolation of four racemic β-decalols gives strong support to this hypothesis.

Decalol							
(I)		(II)		(III)		(IV)	
+	−	+	−	−	+	−	+
+	−	+	−	+	−	+	−
+	−	−	+	+	−	−	+

The writer has noticed that there exists some regular correspondence between the stereochemical configurations of monocyclic hexamethylene derivatives and their physical constants, as in o-dimethylcyclohexane. The cis form, according to the investigation made by F. Eisenlohr[2], shows greater physical constants than the trans-isomer, while the cis-form is unstable towards heat and chemical reagents than the isomer.

	B. p.	d_4^{20}	n_{He}^{20}
Cis-o-Dimethylcyclohexane	$(126.5)_{750}$	0.7822	1.4306
Trans-o-Dimethylcyclohexane	$(124.5)_{755}$	0.7798	1.4299

1. H. Leroux, Compt. rend., **139**, 672 (1904); **140**, 590 (1905); W. Ipatiew, Ber., **40**, 1281 (1907); L. Mascarelli, Chem. Zentr., IV, 1807 (1911); II, 1117 (1912); W. Hückel, Chem. Zentr., III, 766 (1923); Ber., **58**, 1449 (1925); Ann., **441**, 1 (1925); **451**, 109 (1927).
2. Der Molekulare Brechungskoeffizient in der Reihe der Polymethylen Verbindungen (1925).

Such a relation between the physical constants and the stereoisomers of hexamethylene derivatives may be expected to be found in the case of decalols and decalins, and it was noticed by Zelinsky and Turowa-Pollak[1] that cis-decalin was transformed into the trans-isomer by heating with aluminium bromide at 100°. The writer, therefore, was led to believe that the cis-compounds in the bicyclic hexamethylene compounds show, in general, higher values in boiling point, density and refractivity and are more unstable against heat and chemical reagents than the trans-isomers.

The formation of any isomeric compound from naphthalene and naphthols by catalytic hydrogenation may be foreseen from a knowledge of the chemical and physical properties of the stereoisomers in hydronaphthalenes and their derivatives.

By the catalytic reduction of α-naphthol[2] in the presence of reduced nickel heated at 135°-145°, 90 % of tetralin and 10 % of ar-tetralol (10 % were ar- and 90 % ac-compounds) were formed, but the yield of tetralols is raised by employing high pressure, and 3 % tetralin, 30 % ac- and 35 % ar-tetralols result at 150° and under 160 atmospheric pressures of hydrogen. In the same manner the present writer and I. Nishimatsu[3] have obtained three β-decalols with M. p. 105° C ; M. p. 75°C and liquid in form, ac-β-tetralol and ar-β-tetralol by the catalytic reduction of β-naphthol in the presence of reduced nickel heated to 135-140° under ordinary pressure.

	M. p.	B. p.	d_4^{25}	n_D^{25}
Ac-α-Tetralol	—	$(133–135)_{14}$	1.088	1.565
Ar-α- „	69.5°	—	—	—
Ac-β- „	—	$(138–143)_{15}$	1.082	1.554
Ar-β- „	58°–59°	(272–275)	—	—

β-Tetralols having lower physical constants than the α-isomers, were supposed to be more stable against heat and chemicals than the isomers, and the occurrence of tetralols and decalols in the reduction product of β-naphthol, as reported by the writer and Nishimatsu, should be true as a matter of course.

1. Ber., **58**, 1292 (1925).

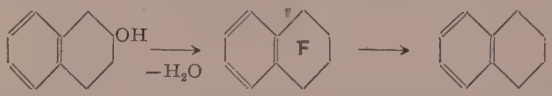
2. S. Komatsu and R. Nodzu, these Memoirs, **6**, 177 (1923); N. Shono, Jour. Chem. Soc. Japan, **50**, 417 (1929).

3. "The Sexagint" a collection of papers dedicated to Prof. Y. Osaka by his pupils in celebration of his sixtieth birthday, 217 (1927).

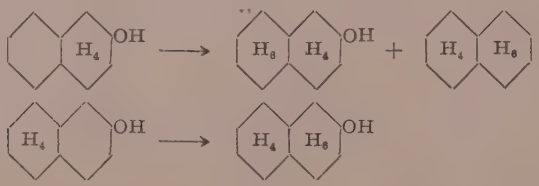
In order to see the effect of temperature and pressure on the formation of these stereo-isomers from β-naphthol, the present investigations were performed, and the experimental results obtained under various conditions are shown in the table.

	Reaction		Mol %			
	Temperature C	Pressure (atmospheres)	Hydrocarbons	Ac-comp.	Ar-comp.	Decalol
(I)	130°–150°	63	—	59.3	40.7	—
(II)	160°	70	—	47.2	51.6	1.2
(III)	190°	57	6.9	41.5	43.2	8.4

When reduction was carried out under conditions (I) and (II) no hydrocarbons were produced, but they were actually isolated from the reaction product formed at the higher temperature (III) and also at high temperature and under ordinary pressure owing to the decomposition of ac-β-tetralol as shown in the following figure:—



The formation of decalol from β-naphthol by reduction below 190° is explained by the conversion of ar-β-tetralol, which is formed simultaneously with ac-β-tetralol and the latter yields hydrocarbons on reduction. This explanation is based on the fact that decalols were formed by the reduction of ar-β-tetralol at 180° and under 67 atmospheric pressures of hydrogen, while the reduction of ac-β-tetralol to decalols was difficult; when the temperature was raised to 270°C, however, it was transformed into hydrocarbons (37 %) and decalols. (63 %).



When the catalytic reduction of β-naphthol was performed below 150°, the ac-compound predominated in the product, but the formation of the ar-compound was favorable at higher temperatures. High pressure has the effect of increasing the amount of the ar-compound formed, as may be seen by comparing the writer's results with those

obtained by A. Brochet and R. Cornubert[1]. In the latter case, the reaction was conducted at 150° and under 15 atmospheric pressures of hydrogen, and 75 % of the ac-compound and 25 % of the ar-isomer were isolated.

All these results shown above lead to the notion that in the hydrogenation of naphthol by the catalytic action of reduced nickel, the reduction of the benzene ring is more greatly facilitated by high temperature and high pressure than that of the phenol ring, naphthol being regarded as a condensed compound of benzene and phenol, or in other words the benzene nucleus in the molecule is more activated than the phenol one under high pressure and temperature to react with activated hydrogen, and the formation of decalols evidently resulted with a fruitful yield because the phenol nucleus is originally more reactive than the benzene nucleus under ordinary conditions.

The β-decalol obtained from ar-tetralol at 180° and under 58 atmospheric pressures of hydrogen was composed of cis-cis-decalol M. p. 105° and some liquid isomer (A) while that obtained from ac-β-tetralol by treating it at 200-270° and under 65 atmospheric pressures of hydrogen was composed only of liquid decalol (B).

		B. p.	d_4^{25}	n_D^{25}
(A)	Liquid-β-Decalol	$(120-132)_{17}$	0.9986	1.5012
(B)	Liquid-β-Decalol	$(129-132)_{17}$	0.9833	1.4944

The proportion of the cis- and the trans-isomers in these two liquid decalols was calculated from the physical constants and also from the physical constants of the decalone produced from decalols by oxidation with chromic acid as follows:

		Cis-comp.	Trans-comp.
(A)	Liquid-β-Decalol	74.7	25.3
(B)	Liquid-β-Decalol	24.2	75.8

The cis compound predominates in decalols prepared from ar-tetralol owing to the stable nature of the compound at lower temperatures, but it will change at high temperature into the stabler trans-isomer.

The transformation of the cis-compound by heat into the trans-isomer was performed by heating 19 gms. of the liquid decalol

1. Bull. Soc. Chim., (4), **31**, 1280 (1922).

containing 74.7 % of the cis- and 25.3 % of the trans-isomers, at 240-260° for 5 hours, under 100 atmospheric pressures of hydrogen in the presence of reduced nickel; trans-cis-β-decalol, M. p. 75°C, liquid-β-decalol and some hydrocarbon were isolated from the reaction product, as will be seen in the table:

	Yield. (gms.)	B. p.	M. p.	d_4^{25}	n_D^{25}
Hydrocarbon	1.7	$(188–190)_{764}$	—	0.8791	1.4721
Liquid-β-Decalol	7.8	$(122–124)_{13}$	—	0.9785	1.4924
Trans-cis-β-Decalol	5	$(122)_{14}$	75°	—	—

The liquid decalol giving trans-decalone only on oxidation with chromic acid, was assumed to be composed of trans-cis- and trans-trans-decalols.

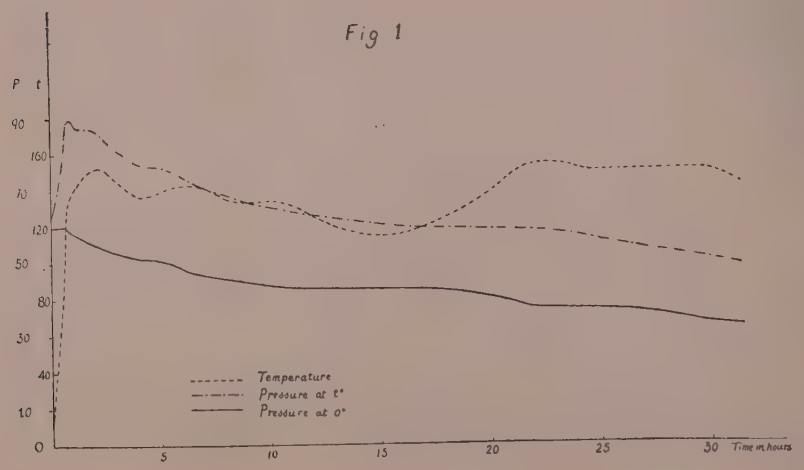
Experimental

Apparatus:—An autoclave of 625 c. c. capacity heated externally by means of electro-resistance was used.

Catalyst:—Reduced nickel obtained by the reduction of nickel oxide derived from nickel nitrate at 290°-320°C with hydrogen gas was used as a catalyst.

Sample:—The β-naphthol used in this experiment contained no sulphur compound as an impurity and showed B. p.=286°; M. p.=122°.

Fig 1



(I) Catalytic Reduction of β-Naphthol

(I):—55 gms. of β-naphthol were reduced at below 150°C under 63 atmospheric pressures of hydrogen at 14° and the fall in the hydrogen pressure during 31 hours was observed to be about 29 atmospheres, as is shown in Fig. 1, which corresponds to a theoretical absorption of 29.8 atmospheric pressures, for saturation of two double bonds in the molecule.

The chemical reaction, as will be seen in Fig. 1, begins at 122°, the melting point of β-naphthol, and the reaction product was a viscous brownish liquid showing $d_4^{25}=1.087$; $n_D^{25}=1.564$. The yield was 51 gms.

It was divided by means of a 10 % caustic potash solution into two parts; 19.3 gms. of the soluble part and 26 gms. of the insoluble, $d_4^{25}=1.083$; $n_D^{25}=1.561$.

The alkali-soluble part was fractionated into 2 parts under 765 mm. pressure:

	Fraction	Yield (gms.)
(1)	272°–277°	17.4
(2)	278°–285°	0.7

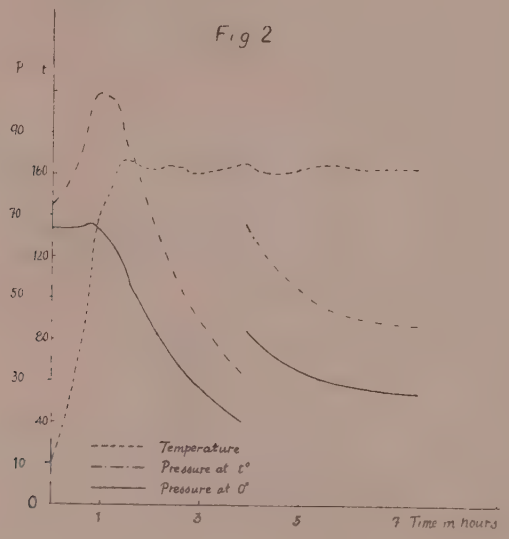
Fraction (2) was composed of unchanged β-naphthol, and fraction (1) consisted mostly of ar-β-tetralol which was purified by recrystallisation from petroleum ether; 15.8 gms. of the purified substance, M. p. =58-59°C, were isolated.

The portion which was insoluble in the alkali solution, containing no trace of hydrocarbon, was purified by distillation under 15 mm. pressure, and 23 gms. of ac-β-tetralol, B. p. $=(143)_{15}$; $d_4^{25}=1.085$; $n_D^{25}=1.5618$, M. R. =44.4 (44.1 for $C_{10}H_{12}OF_3$) were isolated. The yield of the two tetralols was as follows:

	Yield (gms.)	Mol %
Ar-β-Tetralol	15.8	40.7
Ac-β-Tetralol	23.0	59.3

(II):—105 gms. of β-naphthol were reduced at 160° and under 73 atmospheric pressures of hydrogen at 20° for 6 hours, and the fall in the pressure was 64 atmospheres, as may be seen in Fig. 2, which corresponds to 2 mols of hydrogen to saturate two double bonds in the molecule.

105 gms. of the brownish viscous liquid, $d_4^{25}=1.082$; $n_D^{25}=1.560$, were separated into parts, 45.5 gms. of an alkali-soluble substance and 46 gms. of an insoluble substance.



The alkali-soluble part was purified by distillation and recrystallisation from petroleum ether, and 43 gms. of ar-β-tetralol, B. p.$=(270$-$272)_{764}$; M. p.$=59°$, were obtained.

The alkali-insoluble part ($d_4^{25}=1.077$; $n_D^{25}=1.558$) was fractionated into the following two portions under 16 mm. pressure.

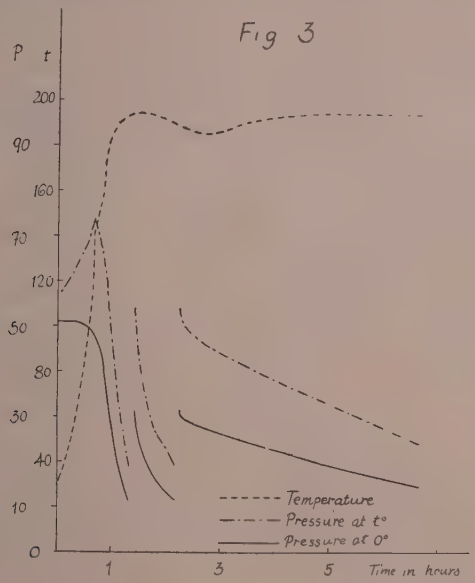
	Fraction 16 mm.	Yield gms.	d_4^{25}	n_D^{25}	Remarks
(1)	130–143°	9	1.051	1.5520	{Ac-β-Tetralol 7.9 gms. {Liquid-β-Decalol 1.1 gms.
(2)	143–146°	34	1.082	1.5588	{Ac-β-Tetralol {M.R.=44.2 (44.1 for $C_{10}H_{12}OF_2$)

The quantity of ac-β-tetralol and liquid-β-decalol in fraction (1), was calculated by means of the refractive power of ac-β-tetralol ($n_D^{\alpha}=1.5588$), liquid-β-decalol ($n_D^{25}=1.5012$).

In the following table, the yield of tetralols and decalol in the reaction products is shown:

	Yield (gms.)	Mol %
Ar-β-Tetralol	43.9	51.6
Ac-β-Tetralol	41.0	47.2
Liquid-β-Decalol	1.1	1.2

(III) :—105 gms. of β-naphthol were reduced at 190° and under 57 atmospheric pressures of hydrogen at 32°. There was a fall of 78 atmospheres in a period of 6 hours, as is shown in Fig. 3.



103 gms. of the reaction product were treated with an alkali solution as usual and 42 gms. of a soluble and 56.5 gms. of an insoluble substance were obtained. From the alkali-soluble part, 37.8 gms. of pure ar-β-tetralol, B.p.=(269-273°)$_{762}$; M. p.=58°C, were isolated.

The alkali-insoluble part, (d_4^{25}=1.060; n_D^{25}=1.5454) was divided by distillation into 4 fractions.

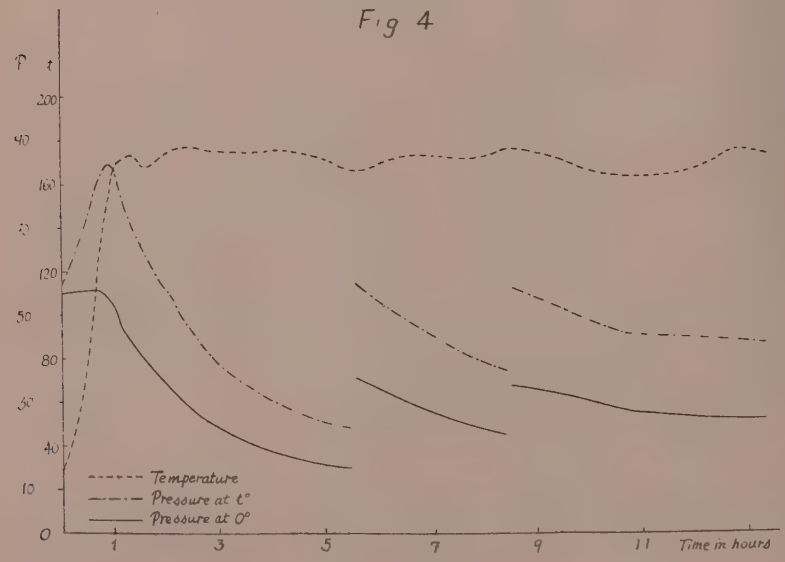
	Fraction 35 mm.	Yield gms.	d_4^{25}	n_D^{25}	Remarks
(1)	95–109	5.4	0.9589	1.5287	Tetralin 4.6 gms. Decalin 0.8 „
(2)	153–163	5.7	1.030	1.5249	Aç-β-Tetralol 2.5 „ Liquid-β-Decalol 3.2 „

	Fraction 35 mm.	Yield gms.	d_4^{25}	n_D^{25}	Remarks
(3)	158–166	12.6	1.053	1.5368	{Ac-β-Tetralol 8.1 gms. {Liquid-β-Decalol 4.5 „
(4)	166–170	25.7	1.079	1.5568	{Ac-β-Tetralol {M.R.=43.8(44.1 for $C_{10}H_{12}OF_3$)

The quantity of tetralin, decalin, ac-β-tetralol and liquid-β-decalol in fractions (1), (2) and (3) was calculated by means of their refractive power (ac-β-tetralol $n_D^{25}=1.5568$; liquid-β-decalol $n_D^{25}=1.5012$; decalin $n_D^{25}=1.4713$[1]; tetralin $n_D^{25}=1.5392$[1]), and the results are shown in the following table:

	Yield (gms.)	Mol %
Hydrocarbons {Tetralin / Decalin	5.4 {4.6 / 0.8	6.9
Liquid-β-Decalol	7.7	8.4
Ac-β-Tetralol	36.3	41.5
Ar-β-Tetralol	37.8	43.2

Fig 4



1. I. Kagehira, Report of the Naval Fuel Depot, Imperial Japanese Navy, **4**, No. 4, 65 (1929).

(II) The Catalytic Reduction of Ar-β-Tetralol

80 gms. of ar-β-tetralol prepared from β-naphthol by catalytic reduction were reduced at 180° and under 58 atmospheric pressures of hydrogen at 15° for 12 hours, and the fall in pressure was observed to be 62.4 atmospheric pressures, as shown in Fig. 4, and 79 gms. of a viscous colourless liquid, $d_4^{25}=1.001$; $n_D^{25}=1.5045$, were produced.

1.7 gms. of unchanged ar-β-tetralol were removed from the reaction product by treatment with an alkali solution, and the insoluble portion consisting of 26 gms. of a white solid substance and 37.3 gms. of a liquid one, was separated into cis-cis-β-decalol, M.p.=104-105°C, by recrystallization from petroleum ether, and liquid-β-decalol, B.p.=$(129\text{-}132)_{17}$; $d_4^{25}=0.9989$; $n_D^{25}=1.5012$; M.R.=45.6 (45.5 for $C_{10}H_{18}O$), by vacuum distillation.

10 gms. of the liquid-β-decalol were dissolved in 30 c.c. of glacial acetic acid, and cooled with ice-water, and 5 gms. of chromic acid solution were added drop by drop. The oxidation product was subjected to steam distillation and 9.2 gms. of an oily substance were isolated, from which 16.9 gms. of semicarbazone were obtained. 9.7 gms. of β-decalone semicarbazone, M. p.=186°C, were obtained by recrystallization from methyl alcohol, which yielded 2.6 gms. of pure β-decalone with the following properties :—

B.p.=$(244\text{-}247°)_{767}$; $d_4^{25}=0.9923$; $d_4^{20}=0.9961$; $n_D^{25}=1.4882$; $n_D^{20}=1.4901$

The proportion of cis- and trans-isomers in this decalone was calculated by means of their density as observed by W. Hückel[1], (cis-β-decalone, $d_4^{20}=1.0029$; trans-β-decalone $d_4^{20}=0.976$), and found to be as follows :—

cis-β-Decalone	74.7 %
trans-β-Decalone	25.3 %

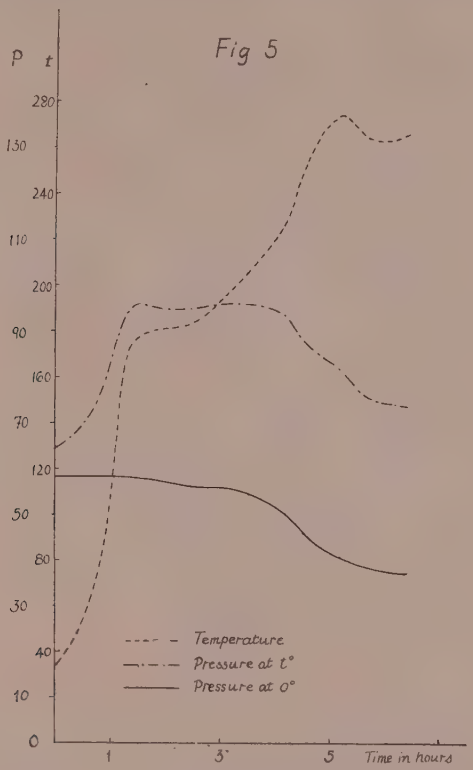
The percentages of cis- and trans-decalols in the writer's sample were ascertained to be 85 % and 15 % respectively, the calculation being based on the proportion of the two decalones.

(III) Catalytic Reduction of Ac-β-Tetralol

32 gms. of ac-β-tetralol, prepared in the previous experiments, were reduced under 65 atmospheric pressures of hydrogen at 35°. As the reaction does not occur below 200°, the temperature was raised

1. Ann., **451**, 126 (1927).

to 270°, and 25.8 atmospheric pressures of hydrogen were consumed in a period of 5 hours, as may be seen in Fig. 5.



29 gms. of the colourless viscous reaction product, (d_4^{25}=0.9492; n_D^{25}=1.4862) were fractionated into the following 3 portions.

	Fraction	Yield gms.	d_4^{25}	n_D^{25}	Remarks
(1)	188–193°	7.5	0.8894	1.4772	{Tetralin 0.7 gm. {Decalin 6.8 gms.
(2)	$(125\text{–}129°)_{17}$	2.4	0.9657	1.4901	{Hydrocarbon 0.6 gm. {Liquid-β-Decalol 1.8 gms.
(3)	$(129\text{–}132°)_{17}$	13.6	0.9833	1.4944	{Liquid-β-Decalol {M.R.=45.6(45.5 for $C_{10}H_{18}O$)

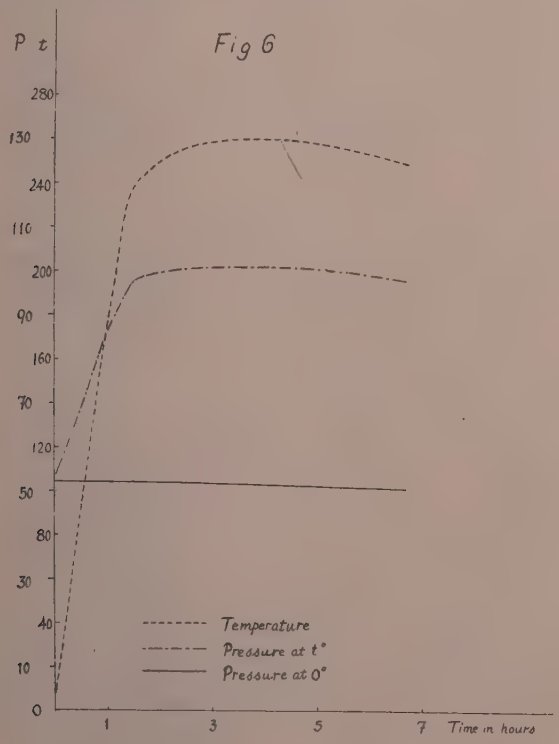
	Yield (gms.)	Mol %
Hydrocarbon	8.1	37 {Decalin 33.8 {Tetralin 3.2
Liquid-β-Decalol	15.4	63

5 gms. of the liquid-β-decalol were oxidised by chromic acid, and 3 gms. of β-decalone semicarbazone, M. p. = 187°C, were obtained, which gave, on hydrolysis, 1.6 gms. of β-decalone, B. p. = $(241\text{-}243)_{765}$, d_4^{25} = 0.9778 ; d_4^{20} = 0.9825 ; n_D^{25} = 1.4829 ; n_D^{20} = 1.4846).

The quantity of cis- and trans-isomers in the decalone was calculated and found to be 24.2 % and 75.8 % respectively, and consequently the liquid decalol was assumed to consist of 24.2 % cis- and 75.8 % trans-isomers.

(IV) The Catalytic transformation of Cis-β-Decalol into Trans-β-Decalol

19 gms. of the liquid-β-decalol prepared in experiment (IV), were kept in the presence of reduced nickel at 240-260° and under 100 atmospheric pressures of hydrogen for 7 hours and some fall in pressure was noticed, as may be seen in Fig. 6.



The reaction product was recrystallized from petroleum ether and found to be composed of 5 gms. of trans-cis-β-decalol, M. p.$=75$°C, hydrocarbon and liquid-β-decalol.

	Yield gms.	B. p.	d_4^{25}	d_4^{20}	n^{25}	n_D^{20}	Remarks
Hydro-carbon	1.7	$(188\text{-}190)_{764}$	0.8791	0.8824	1.4721	1.4742	{Cis-Decalin 40.5 % {Trans-Decalin 59.5 %
Liquid-β-Decalol	7.8	$(122\text{-}124)_{15}^{\circ}$	0.9785		1.4924		{M.R.$=45.7$ {(45.5 for $C_{10}H_{18}O$)
Trans-cis-β-Decalol	5.0	$(122)_{14}$					M.p.$=75$°C

The proportion of cis- and trans-decalin in the hydrocarbon was calculated from their refractive power (cis-decalin $n_D^{20}=1.4795$, trans-decalin $n_D^{20}=1.4706$ as stated by Willstätter[1]) and found to be 41 % and 59 % respectively.

5 gms. of the liquid-decalol were converted by the usual method into 3.3 gms. of decalone semicarbazone, M. p.$=187$°, which yielded 1.2 gms. of β-decalone; B. p.$=(239\text{-}242°)_{764}$, $d_4^{25}=0.9717$; $d_4^{20}=0.9763$; $n_D^{25}=1.4818$; $n_D^{20}=1.4831$.

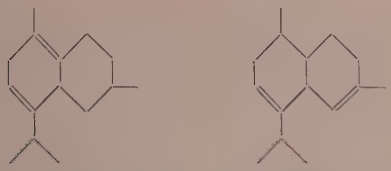
The β-decalone thus obtained, having the same properties as the trans-β-decalone obtained by W. Hückel ($d_4^{20}=0.976$; $n_D^{20}=1.4822$)[2], was assumed to consist only of the trans-compound.

Part II

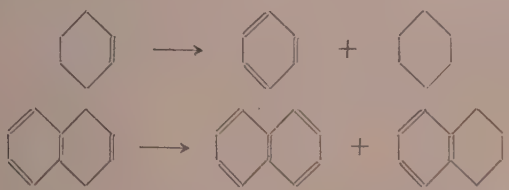
Catalytic Oxidation-Reduction of Hydronaphthalenes and Sesquiterpenes

The investigations hitherto performed by many investigators to determine the chemical structure of bicyclic sesquiterpenes by converting them into naphthalene derivatives by oxidation, afford no evidence of the position of the double bonds in their molecules[3]. This may be seen from the experiments made by L. Ruzicka and M. Stoll on the structure of cadinene, for which two constitutional formulae are seen to be possible from the study of the oxidation products:—

1. Ber., **57**, 683 (1924).
2. Loc. cit.
3. O. Aschan, Naphthenverbindungen Terpene und Campherarten (1929), 1; O. Wallach, Ann., **238**, 87 (1887); F. W. Semmler u. K. G. Jonas, Ber., **47**, 2076 (1914); F. W. Semmler u. W. Jakatowicz, Ber., **47**, 2258 (1914); L. Ruzicka u. J. Meyer u. M. Mingazzini, Helv., **5**, 345 (1922); L. Ruzicka u. M. Stoll, Helv., **7**, 84 (1924).

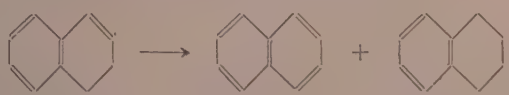


This doubt as to the chemical structure of bicyclic terpenes might be partly cleared up if the catalytic oxidation-reduction method, which was proposed by N. Zelinsky[1] and then studied by other chemists were applied. In this method, cyclohexene and $\triangle^2$-dihydronaphthalene in the presence of palladium or platinum are converted into benzene and cyclohexane, and naphthalene and tetralin respectively.



The reliability of this method for the determination of the structure of such compounds as sesquiterpenes, was investigated by the writer by applying it to hydronaphthalenes.

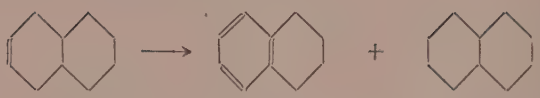
When, $\triangle^1$-dihydronaphthalene was passed over palladium asbestos heated to 250-300°C in an atmosphere of CO_2, it was found that naphthalene and tetralin were present in the reaction product, this being proved by determination of the physical constants and by forming derivatives after they had been isolated by distillation.



B. p.	206.5–207°	204–206°
d_4^{25}	0.9931	0.974
n_D^{25}	1.5789	1.552

Cis-octalin (cis-octahydronaphthalene) similarly treated and heated at 200-220°C formed tetralin and trans-decalin, the physical constants of which were also studied.

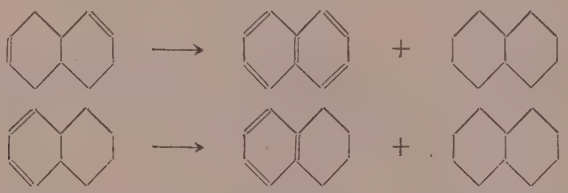
1. N. Zelinsky u. G. Pawlow, Ber., **57**, 1066 (1924).



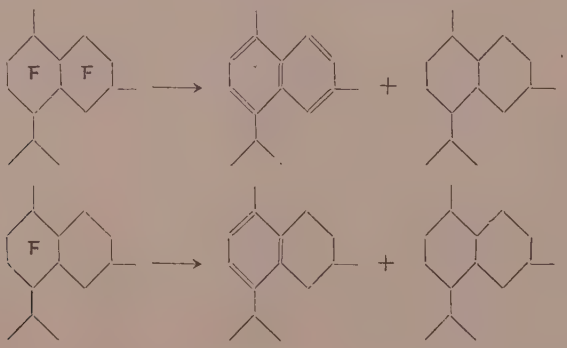
B. p.	191–192°	198–203°	186–188°
d_4^{25}	0.9011	0.954	0.8723
n_D^{25}	1.4912	1.514	1.4719

The occurrence of trans-decalin in the reaction product was explained by assuming that the cis-isomer as the writer has before maintained[1] was converted at high temperature in the presence of a catalyst into the trans-compound.

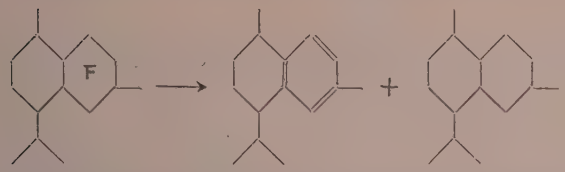
From these experimental results it can easily be anticipated that hydronaphthalene, in which two double bonds are distributed in each ring of the molecule, will tend to be converted by the catalytic oxidation-reduction into naphthalene and decalin, while the compound which contains two double bonds in the same ring will form tetralin and decalin.



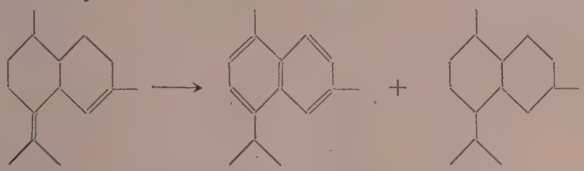
In the same manner, sesquiterpenes of the following-structural formulae may be expected to be converted into cadalene and its hydrocompounds :



1. See Part I, experiment (IV).



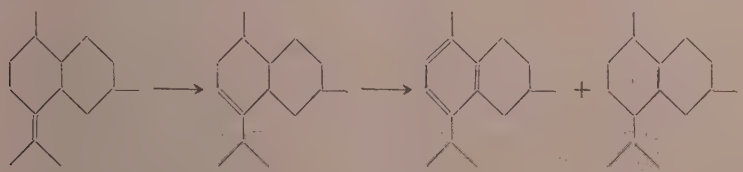
The fact that the sesquiterpene isolated from Japanese cedar oil (Cryptomeria japonica oil, Sugi oil)[1] was converted by catalytic oxidation-reduction at 280-300°C in the presence of palladium asbestos into cadalene and decahydrocadalene, as was confirmed by measuring the physical constants of their isolated reaction products and also by forming cadalene picrate, is evidence in favour of the structure formulae (I) which we proposed for sesquiterpene and which was discussed previously from the study of its chemical reactions.[1]



I

B. p.	$(108\text{–}114°)_{4.5}$	$(120\text{–}132°)_{4.5}$	$(97\text{–}100°)_4$
d_4^{25}	0.9150	0.936	0.8812
n_D^{25}	1.5085	1.530	1.4758

Also, the catalytic oxidation-reduction of octahydrocadalene $C_{15}H_{26}$, derived from the sesquiterpene alcohol of Japanese cedar oil[1] gives strong support to the chemical structure (II) suggested for the hydrocarbon, since decahydrocadalene and tetrahydrocadalene were formed and confirmed from the physical constants, as may be seen in the table:



II

B. p.	$(102\text{–}106)_4$		$(108\text{–}118)_4$	$(97\text{–}100°)_4$
d_4^{25}	0.8944		0.907	0.8730
n_D^{25}	1.4915		1.506	1.4745

1. S. Kimura and S. Mizoshita, J. C. S. Japan, **51**, 518 (1930).

Experimental

1. $\triangle^1$-Dihydronaphthalene

10 gms. of ac-β-tetralol, B. p.$=(143)_{15}$; $d_4^{25}=1.0850$; $n_D^{25}=1.5618$, prepared by catalytic reduction of β-naphthol under high temperature and pressure[1], were treated with 10 gms. of dry potassium hydroxide at 195-200°C for 15 minutes in accordance with the directions given by E. Bamberger and W. Lodter[2]. The reaction product was extracted with ether, washed with water, dried, and then distilled. 7.5 gms. of a liquid, B. p.$=(207\text{-}215)_{764}$; $d_4^{25}=0.994$; $n_D^{25}=1.578$,were obtained. $\triangle^1$-dihydronaphthalene purified by distillation shows B. p.$=(206.5\text{-}207)_{764}$; M. p.$=-9$ C; $d_4^{25}=0.9931$; $n_D^{25}=1.5789$ and yields dihydronaphthalene dibromide, M. p.$=68°$.

These experimental results obtained with the compound show fair agreement with the properties of $\triangle^1$-dihydronaphthalene mentioned by V. Auwers[3] and R. Willstätter u. V. L. King[4].

	B. p.	M. p.	d_4^{20}	n_D^{20}	M. p. of Dihydronaphthalene Dibromide
Auwers	$(89)_{18}$	—	0.997	1.5832	68°C
Willstätter & King	$(84\text{-}85)_{12}$	−9°	0.997	—	—

2. Catalytic Oxidation-Reduction of $\triangle^1$-Dihydronaphthalene

Palladium asbestos[5] was spread in a glass tube about, 1 metre long and heated to 250-300°. 12 gms. of the sample were passed over this with dry carbon dioxide, by means of a capillary tube in a period of 2.5 hours, the reaction product consisting of 6.5 gms. of solid substance and 1 gm. of a liquid. The former was confirmed to be naphthalene from its M. p.$=80°$ and other properties after recrystallisation.

The latter, showing the physical constants $d_4^{25}=0.978$; $n_D^{25}=1.559$, was distilled on metallic sodium and 0 5 gm. of a hydrocarbon having the properties: B.p.$=(204\text{-}206°)_{765}$; $d_4^{25}=0.974$; $n_D^{25}=1.552$ were isolated.

1. See Part I, experiment (I).
2. Ber., **23**. 208 (1890).
3. Ber., **46**, 2988 (1913).
4. Ber., **46**, 527 (1913).
5. Zelinsky u. Borisoff, Ber., **57**, 150 (1924).

These constants show fair agreement with those of tetralin[1] (d_4^{25} = 0.9675; n_D^{25} = 1.5392) prepared by Kagehira.

3. Cis-Octalin

Cis-octalin was prepared from decalol by the method which Sendrens[2] used for the preparation of cyclohexene from cyclohexanol; a few drops of $H_2SO_4 3H_2O$ were added to 10 gms. of cis-cis-β-decalol, M. p. = 104-105°C, in a distillation flask and heated to 100-120°, and the hydrocarbon thereby produced was distilled out with water. The yield was 7 2 gms. It showed B. p. = 191-195°; d_4^{25} = 0.912; n_D^{25} = 1.492. 6.3 gms. of pure cis-octalin, B. p. = $(191\text{-}192°)_{760}$; d_4^{25} = 0.9110; n_D^{25} = 1.4912; M. R. = 43.3 (calc. for $C_{10}H_{16}F_1$ = 43.5) were isolated by distillation with metallic sodium. These properties agree with those (B. p. = $(194)_{771}$; d_4^{20} = 0.909; n_D = 1.4912) of cis-octalin prepared by F. Eisenlohr and R. Polenski[3].

4. Catalytic Oxydation-Reduction of Cis-Octalin

9 gms. of the cis-octalin were heated at 200-220°C in the presence of a catalyst for one and a half hours, and 6.5 gms. of the reaction product, d_4^{25} = 0.905; n_D^{25} = 1.495, were obtained. This reaction product was fractionated into the following three portions:

	B. p. 760 mm.	Yield (gms.)	d_4^{25}	n_D^{25}
(1)	190–191	1.3	0.893	1.486
(2)	191–198	3.0	0.900	1.491
(3)	198–203	1.2	0.954	1.514

Trans-decalin: Fraction (1) was treated with conc. sulphuric acid to remove unsaturated compounds, distilled on metallic sodium, and 0.7 gm. of the hydrocarbon of properties, B. p. = $(186\text{-}188)_{760}$; d_4^{25} = 0.8723; n_D^{25} = 1.4719; M. R. = 44.3 (calc. for $C_{10}H_{18}$ = 44.0) was obtained. These properties agree with those of trans-decalin obtained by Willstätter[4] and W. Hückel[5].

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1. Loc. cit.
2. Compt. rend., **177**, 1183 (1923).
3. Ber., **58**, 1449 (1925).
4. Ber., **57**, 683 (1924).
5. Ann., **441**, 42 (1925).

Tetralin: Fraction (3) was assumed to consist of tetralin from the physical constants.

5. Decahydrocadalene (Tetrahydrocadinene)

40 grms. of the sesquiterpene (B. p.$=(108\text{-}114^{\circ})_{4.5}$; $d_4^{25}=0.9150$; $n_D^{25}=1.5085$; $[\alpha]_D=-22.4$), isolated by the writer from Japanese cedar oil[1], were reduced with hydrogen in the presence of reduced nickel under 90 atmospheric pressures and at 150°, and 37 grms. of reaction product (B. p.$=(109\text{-}122^{\circ})_6$; $d_4^{25}=0.894$; $n_D^{25}=1.491$) were obtained. 5 grms. of this reaction product, treated with conc. sulphuric acid, as usual, and then distilled with metallic sodium under diminished pressure yielded 3 grms. of a hydrocarbon with the following properties:— B. p.$=(92\text{-}95^{\circ})_3$; $d_4^{25}=0.8756$; $n_D^{25}=1.4780$; M. R.$=67.2$ (calc. for $C_{15}H_{28}=67.1$). These constants agree well with those of the decahydrocadalene prepared by L. Ruzicka and M. Mingazzini[2].

6. Catalytic Oxidation-Reduction of Sesquiterpene

12 grms. of sesquiterpene isolated from Japanese cedar oil, were subjected to catalytic oxidation-reduction by heating at 280-300°C for 2 hours in an atmosphere of dry carbon dioxide, and 11 grms. of reaction product ($d_4^{25}=0.922$; $n_D^{25}=1.522$) were obtained. This was fractionated under 4.5 mm. pressure.

	B. p. 4.4 mm.	Yield (grms.)	d_4^{25}	n_D^{25}
(1)	104-111°	1.1	0.899	1.498
(2)	111-120°	4.8	0.911	1.509
(3)	120-132°	4.3	0.936	1.530

Decahydrocadalene: Fraction (1) was distilled under reduced pressure with metallic sodium after removing the unsaturated hydrocarbon with conc. sulphuric acid, and a hydrocarbon having the properties, B. p.$=(97\text{-}100)_4$; $d_4^{25}=0.8812$; $n_D^{25}=1.4758$, was obtained. These properties indicate that the fraction consists of decahydrocadalene.

Cadalene: Fraction (3) was assumed to consist of cadalene, the assumption being justified by reference to its physical constants and also by the isolation of cadalene picrate,[3] M. p.$=114\text{-}115^{\circ}$.

1. Loc. cit.
2. Helv., **5**, 357 (1922).
3. Helv., **4**, 508 (1921)

7. Catalytic Oxidation-Reduction of Dihydrosesquiterpene $C_{15}H_{26}$

Dihydrosesquiterpene prepared by the dehydration of a dihydro-compound derived from the sesquiterpene alcohol isolated from Japanese cedar oil, shows the following properties:—B. p.$=(102\text{-}106°)_4$; $d_4^{25}=0.8944$; $n_D^{25}=1.4915$; M. R.$=66.4$ (calc. for $C_{15}H_{26}F_1=66.6$). It was treated at 300-320°C for about 40 minutes in the presence of a catalyst and gave 1.9 gms. of a reaction product, $d_4^{25}=0.895$; $n_D^{25}=1.500$. This was fractionated under 4 mm. pressures into the following two portions:

	B. p. 4 mm.	Yield (gms.)	d_4^{25}	n_D^{25}
(1)	(97–108)	1.5	0.884	1.489
(2)	(108–118)	0.5	0.907	1.506

Decahydrocadalene: Fraction (1) on being treated with conc. sulphuric acid, and distilled on metallic sodium, yielded decahydrocadalene having the constants; B. p.$=(97\text{-}100)_4$; $d_4^{25}=0.8730$; $n_D^{25}=1.4745$.

Tetrahydrocadalene: Fraction (2) was assumed from the physical constants to consist of tetrahydrocadalene.

In conclusion, the writer wishes to express his hearty thanks to Professor S. Komatsu of Kyoto Imperial University, under whose kind direction and encouragement the experiments were performed.

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